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ORIGINAL PAPERS

EFFECT OF ZIRCONIA IN ENAMELS FOR SHEET STEEL[1]

By H. G. Wolfram

ABSTRACT

This paper deals with the results obtained from a study of the effect of additions of zirconium oxide to enamels for sheet iron and steel. The work includes additions of the zirconia to the raw smelter batch of both the ground and cover enamels, also the substitution of the zirconia for tin oxide in the mill batch. Several tests were used to determine its effect on some of the properties of the enamels, such as resistance to impact, thermal shock and acid.

1. Introduction

The every day use of enameled articles in the kitchen requires strong enamels, of good appearance and resistant to weak acids, impact and thermal shock. At the present time there is very little specific data at hand on the use of zirconia in enamels. Staley[2] in his paper entitled "Some Relations of Composition to Solubility of Enamels in Acids" states that zirconia and titanium oxide when substituted separately for small amounts of silica increase the resistance of various enamels to attack by acids. The zirconia is the most effective.

Fritz Kraze[3] in "Zirconium Fluoride in Glazes and Enamels" gives no specific data in his article but says that zirconia makes a stronger enamel which is more resistant to acids. He states that zirconium fluoride enamels display an astonishing elasticity, resisting rapid heating and cooling without injury. Zirconium gives considerable range when used with colors. Considerable zirconium makes a refractory frit and can be substituted in the mill for making opaque white enamels. In this substitution the action of the zirconium is mechanical and has a different opacifying effect than when acted upon by the fluorine in the fritting process.

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[1] This paper is based upon the results obtained by the author in preparation of a thesis to meet the requirements for the degree of B.Sc. in Ceramic Engineering at the University of Illinois, June, 1923. Received November 3, 1923.

[2] H. F. Staley, *Jour. Amer. Ceram. Soc.*, **4** [9], 703 (1921).

[3] Fritz Kraze, *Ber. der Deut.*, **3,** 3 (June), (1922).

Wenning[1] on "Zirconia in Sheet Iron Enamels" gives a short review of his work. A replacement up to 10% by zirconia of silica and alumina changes the working properties of the enamel very little. High replacements give viscous enamels. Enamels containing up to 10% zirconia are more elastic and test to be stronger enamels with better adhesion to the steel.

Wenning also says that zirconia when substituted in the mill formulas of low fluoride enamels gives a whiter enamel with opacity approaching very closely to that of tin oxide enamels. Such enamels are more acid resisting due to their low fluoride content. He summarizes by saying that enamels containing zirconia are more resistant to mechanical and thermal shock and acid. The zirconia is not affected by reducing furnace heat.

Staley[2] in "Materials and Methods for Cast Iron Wares" states that for a given opacity it is necessary to use slightly larger amounts of zirconia than tin oxide.

Grunwald[3] in his book gives a short review of the effect of zirconia on opacity of enamels; nothing definite is stated except that very pure zirconia increases the opacity slightly.

Morgan and Charles, Jr.[4] in their thesis "The Development of a Reflector Enamel" say that zirconia is not satisfactory as a substitute opacifier for tin oxide.

Danielson and Frehafer[5] in their paper "Opacifying Effect of Tin Oxide and Its Substitutes" state that zirconium oxide is nearly as good as tin oxide itself.

The above references point favorably toward the improvement of kitchen ware enamels by the use of zirconia. The following work was carried on in order to obtain definite results and data on its use.

2. Plan of Investigation

This investigation is concerned with the essential properties of kitchen ware enamels, namely, strength, resistance to acid and to thermal shock, and opacity. For the purpose of getting useful results, typical commercial base enamels were used.[1] Additions of zirconia were made both in the smelter and mill batches for the cover coats and in the smelter batch for the ground coats. The base ground coat No. 1 was used, also additions of 2.5% zirconia to the base smelter formula for No. 2, and 5.0% zirconia to the base formula for No. 3.

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[1] W. F. Wenning, *Bull. Amer. Ceram. Soc.*, **6** [5], 102 (1923).

[2] H. F. Staley, Bur. Stand., *Tech. Paper* **142,** 57.

[3] Julius Grunwald and H. H. Hodgson, "Raw Materials for the Enamel Industry," 129 (1912).

[4] Morgan and Charles, Jr., Thesis, Univ. Ill., 34 (1920).

[5] R. R. Danielson and M. K. Frehafer, *Jour. Amer. Ceram. Soc.*, **5,** 634 (1923).

Cover enamel Series A was made by additions of 2.5% and 5.0% zirconia to the smelter batch of the base formula. Another series (B) consisted of the base enamel A with 4.0% and 8.0% substitutions to the mill batch of zirconia for tin oxide.

The zirconia used was a commercial product analyzing 96% zirconia.

With this procedure there were three ground coats with five cover coats to be applied on each, giving fifteen different combinations.

3. Preparation of Enamels

1. A typical commercial ground coat was used in this investigation, namely:

	Batch weight
Borax	32.0
Feldspar	29.0
Quartz	19.0
Soda ash	9.0
Sodium nitrate	5.0
Fluorspar	4.7
Cobalt oxide	0.8
Manganese oxide	0.4
	99.9

The raw materials were fritted by heating to perfect fusion (determined by drawing a thread free from knots) in a crucible and pouring into cold water.

The frit was ground in approximately ten pound batches in a ball mill with constant mill addition of 8%, 1.75% borax (sol.) and 50% water. The additions of zirconia were made in the raw frit batch.

2. The base white enamel used was:

	Batch weight A-1
Borax	25.5
Feldspar	25.0
Quartz	21.0
Soda ash	3.5
Sodium nitrate	3.0
Cryolite	14.0
Antimony oxide	3.0
Zinc oxide	5.0
	100.0

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[1] R. R. Danielson, *Jour. Amer. Ceram. Soc.*, **3** [12], 961 (1923).

The raw materials were fritted by the drop frit method. Two series were made up; the first series A consisted of the base enamel and additions of zirconia in the raw frit batch; the second series B consisted of the base enamel A with the zirconia substituted in the mill batch to replace tin oxide. In series A 7% tin oxide was used in the mill. In all cases a constant mill addition of 6.0% clay, 0.25% magnesium carbonate and 60% water was used.

3. The kitchen ware upon which the enamel was applied consisted of six-inch commercial saucers. They were prepared by first scaling and then pickling in an 8% solution by weight of hydrochloric acid. The enamel was applied by the usual dipping method. The enamel after being "set up" showed no signs of settling and worked very well during the dipping process.

4. The enameling was accomplished in a small muffle furnace fired by city gas. The firing data are given in Tables I and II.

TABLE I

GROUND COATS

No.	Zirconia in smelt batch, %	Temp. of burning °C	Time, sec.
1	...	930	50
2	2.5	930	60
3	5.0	930	70

TABLE II

COVER COATS

Series	On ground No.	Temp. of burning		Time, sec.	
		1st coat	2nd coat	1st coat	2nd coat
A_1	1	820	850	50	90
A_1	2	850	850	60	100
A_1	3	850	850	75	110
A_2	1	850	850.	60	70
A_2	2	850	850	60	70
A_2	3	850	850	65	80
A_3	1	850	850	40	70
A_3	2	850	870	55	75
A_3	3	850	890	60	75
B_1	1	850	870	50	60
B_1	2	850	870	60	70
B_1	3	850	880	75	75
B_2	1	850	890	60	60
B_2	2	850	890	70	75
B_2	3	850	890	75	80

It is quite evident from the above data that the zirconia has a hardening effect upon the enamel. The increase in temperature and time for maturity with increase of zirconia in most cases bears out this fact. An increase in viscosity with increasing zirconia was also noted in the smelting process both in the ground coats and cover enamels, but no data was obtainable, due to the varying conditions of that process.

The samples were very satisfactory in color and gloss. The surfaces were smooth and free from pinholes, fish scale and blisters.

4. Tests of Ware

Impact Test.—This test was carried on by use of the Bureau of Standards method and with apparatus suggested by the Bureau and shown in Figure 1. The piece was centered on the block and impact applied at the center, starting at one-tenth of a foot-pound and increasing in increments of twenty-five thousandths of a foot-pound. Failure was accepted when the enamel chipped over an area at least 0.25 inch in diameter.

The results of the impact tests are shown in Table III.

By plotting curves for the averages of the tests, as in Figs. 2 and 3, it is very easy to compare the effects of the zirconia on both the ground and cover coats.

1. **Ground Coats.**—Increasing amounts of zirconia in the ground coats up to 2.5% increased the resistance to impact in all cases. Further increase in zirconia decreased the resistance where the A series of cover coats was used and showed no beneficial effects where the Series B (4 and 8% additions to the mill batch) was used.

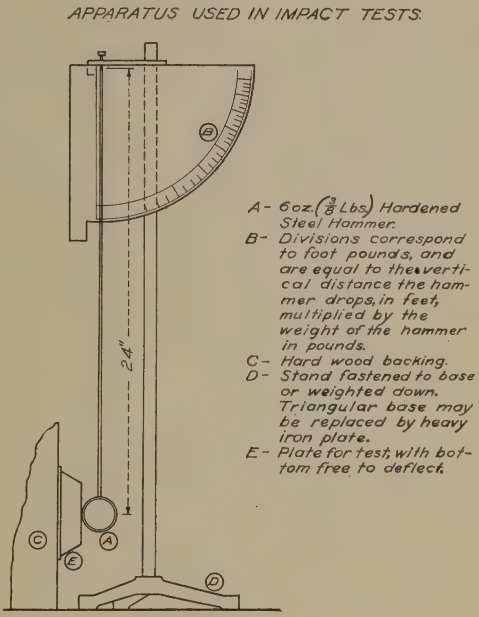
APPARATUS USED IN IMPACT TESTS.
B
24"
A
C
E
D
A - 6 oz. (3/8 Lbs.) Hardened Steel Hammer.
B - Divisions correspond to foot pounds, and are equal to the vertical distance the hammer drops, in feet, multiplied by the weight of the hammer in pounds.
C - Hard wood backing.
D - Stand fastened to base or weighted down. Triangular base may be replaced by heavy iron plate.
E - Plate for test, with bottom free to deflect.

Fig. 1.

2. **Cover Enamels.**—Increasing amounts of zirconia in the smelter batch of the cover enamels increased the resistance to impact in the cases where Nos. 1 and 2 ground coats were used. It gave a slight decrease and then a decided increase where No. 3 ground coat was used. Increased zirconia increased the resistance in the Series B where the zirconia was added at the mill. It is quite evident that the compositions of the ground coats and cover coats, also the combinations of the two, play an important part in the results obtained.

TABLE III

IMPACT TESTS—GROUND COAT NO. 1

Foot-pounds

Trial	0.100	0.125	0.150	0.175	0.200	0.225	0.250	0.275	0.300	0.325	Ft.-lbs., Average
A-1 White											
1	No action	No action	No action	Slight crazing	Crazing	Fail					
2				Slight crazing	Fail						0.209
3				Slight crazing	Fail						
A-2											
1				No action	Slight crazing	Fail					
2					No action	Crazing	Fail				0.259
3						Crazing	Crazing	Crazing	Fail		
A-3											
1				No action		Crazing	Fail				
2						No action	Crazing	Crazing	Fail		0.283
3						No action	No action	Slight crazing	Fail		
B-1											
1					Fail						
2					No action	Crazing	Fail				0.225
3						Fail					
B-2											
1						No action	Fail				
2							Fail				0.267
3							Crazing	Crazing	Fail		

TABLE III (*Continued*)

IMPACT TEST—GROUND COAT NO. 2

Trial	0.100	0.125	0.150	0.175	0.200	0.225	0.250	0.275	0.300	0.300	Ft.-lbs., Average
A-1 White	No action	No action	No action	No action	No action	No action					
1							No action	Fail			
2							Crazing	Fail			0.283
3							Crazing	Crazing	Fail		
A-2											
1							Crazing	Crazing	Fail		
2							Crazing	Crazing	Fail		0.300
3							Crazing	Crazing	Fail		
A-3											
1							No action	Crazing	Crazing	Fail	
2							No action	No action	Crazing	Fail	0.317
3							No action	No action	Fail		
B-1											
1							No action	Crazing	Fail		
2							No action	Fail			0.285
3							No action	Fail			
B-2											
1							No action	No action	Crazing	Fail	
2							No action	No action	Fail		0.300
3							No action	Fail			

TABLE III (*Continued*)

IMPACT TESTS—GROUND COAT NO. 3

Trial	0.100	0.125	0.150	0.175	0.200	0.225	0.250	0.275	0.300	0.325	Ft.-lbs. Average
A-1											
1	No action	No action	No action	No action	No action	No action	No action	No action	Fail		
2						Crazing	Fail				0.275
3						No action	Crazing	Fail			
A-2											
1						No action	No action	Crazing	Fail		
2						Crazing	Fail				0.267
3						Crazing	Fail				
A-3											
1						No action	No action	Fail			
2							No action	Crazing	Fail		0.291
3							No action	Crazing	Fail		
B-1											
1							Crazing	Fail			
2							Crazing	Crazing	Fail		0.284
3							Crazing	Fail			
B-2											
1							No action	Crazing	Fail		
2							No action	Crazing	Fail		0.300
3							No action	Crazing	Fail		

Resistance to Thermal Shock

The plan of investigation of the resistance to thermal shock was in accordance with a method used in some work at the Bureau of Standards, with slight variations suggested by C. W. Parmelee. The ware was placed in an oven of constant temperature of 100°C and quenched five times in cold water. This procedure was repeated at increasing temperature increments of 25°C until failure occurred. Failure was accepted when the enamel chipped off the body of the ware, differentiating from the bead.

After placing the ware in the heated oven, the temperature dropped decidedly. In order to insure perfect conditions, the ware was allowed to remain in the oven from fifteen to twenty minutes after the oven again reached the proper temperature before quenching.

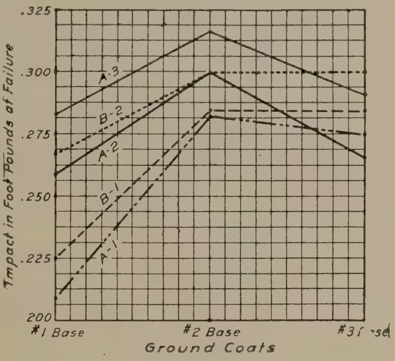

FIG. 2.—Effect of zirconia on resistance of ground coats to impact.

Results are shown in Table IV, and graphically in Figs. 4 and 5.

The increase of zirconia in the ground coats gave a decided decrease in the resistance to thermal shock except in two cases. When A-1 cover coat was used on No. 2 ground coat, there was a decrease in resistance and when used on No. 3 ground coat, the resistance became normal again. There was no beneficial effect noted when B-1 cover coat was used.

When zirconia was increased in the cover coat smelter batches, part of them showed an increase in resistance, part of them no beneficial effect, while in the cases where the zirconia was added to the mill a decided increase in resistance was noted.

From the results obtained it was judged that for an increase of resistance to thermal shock it was best to add the zirconia to the mill batch of the cover coats only.

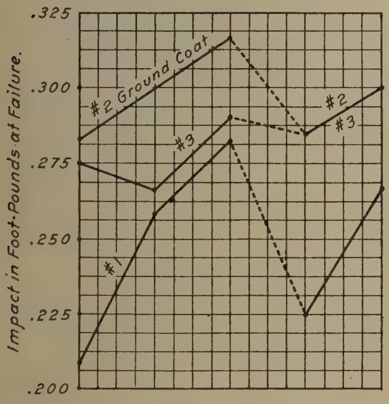

FIG. 3.—The effect of zirconia on resistance of cover enamels to impact.

Resistance to Acid.—The resistance of the ware to solubility in acids was tested by using a cold 1% solution by weight of acetic acid. This solution was placed in the saucer and the ware was examined hourly for failure. Failure was accepted when the ware showed a decided loss of gloss.

TABLE IV

GROUND COAT No. 1

	Trial	100°C	125°C	150°C	175°C	200°C
A-1	1	No action	No action	No action	Crazing	
	2			No action	Failure	
	3			No action		
	4			No action		
	5			Crazing		
A-2	1			No action	Crazing	
	2			No action	Crazing	
	3			No action	Failure	
	4			No action		
	5			Crazing		
A-3	1			No action	Crazing	
	2				Crazing	
	3				Failure	
	4					
	5					
B-1	1				Crazing	
	2				Crazing	
	3				Failure	
	4					
	5				No action	No action
B-2	1				No action	No action
	2				No action	No action
	3				No action	Crazing
	4				No action	Crazing
	5				No action	Failure
	6					

GROUND COAT No. 2

	Trial	100°C	125°C	150°C	175°C	200°C
A-1	1	No action	No action	No action		
	2			No action		
	3			Crazing		
	4			Crazing		
	5			Failure		
A-2	1			No action	Crazing	
	2				Crazing	
	3				Failure	
	4					
	5					
A-3	1				Crazing	
	2				Failure	
	3					
	4			Crazing		
	5			Crazing		
B-1	1				Crazing	
	2				Crazing	

TABLE IV (*Continued*)

	3				Failure	
	4					
	5					
B-2	1			No action	No action	Crazing
	2				No action	Crazing
	3				No action	Crazing
	4				No action	Failure
	5				No action	

GROUND COAT NO. 3

A-1	1	No action	No action	No action	Crazing	
	2			No action	Failure	
	3			No action		
	4			No action		
	5			Crazing		
A-2	1			No action	Failure	
	2			No action		
	3			No action		
	4			Crazing		
	5			Crazing		
A-3	1			No action		
	2			No action		
	3			Crazing		
	4			Failure		
	5					
B-1	1			No action	No action	
	2				Crazing	
	3				Failure	
	4					
	5					
B-2	1				No action	Failure
	2				Crazing	
	3				Crazing	
	4				Crazing	
	5				Crazing	

TABLE V

RESISTANCE TO 1% ACETIC ACID SOLUTION

Cover coat	Hours of loss of gloss
A-1	First
A-2	First
A-3	First
B-1	Second
B-2	Second

There was no beneficial action obtained by increasing the zirconia in the smelter batch of the cover coats. All of this ware failed the first hour. Some benefit was obtained by substituting the zirconia in the mill batch for the tin oxide.

The Effect of Zirconia on Opacity.—A comparative visual examination only was used to determine the effect on opacity of increasing the zirconia. In the A series, where tin oxide was a constant addition to the mill, no benefit was obtained although no difference could be detected between the A-1 base enamel and the others.

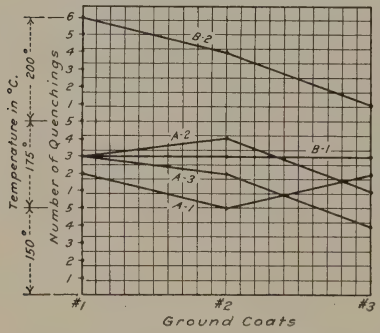

FIG. 4.—The effect of zirconia on resistance of ground coats to thermal shock.

Series B where zirconia was added at the mill to replace the tin oxide, gave an interesting comparison. It was found that B-1, 4% addition of zirconia to replace 7% of tin oxide, gave an enamel equally as white as the tin enamel but lacking in covering power. The B-2 cover coat, with 8% addition of zirconia replacing 7% tin oxide, gave an enamel equally as white as tin with an equal or better opacity.

5. Conclusions

It is plain that the effects produced by the zirconia are dependent upon the composition of the enamel and upon the combination of cover and ground coats.

1. Zirconia additions to the smelter batch increased the time of smelting. All additions of zirconia make the enamel more viscous and thus increase the time of burning.

2. Increasing additions of zirconia to the ground coat smelter batch increases the resistance to impact.

Increasing additions to the cover coat smelter batch gave the best results and highest resistance although increasing amounts, when substituted for tin oxide in the mill, gave increasing resistance.

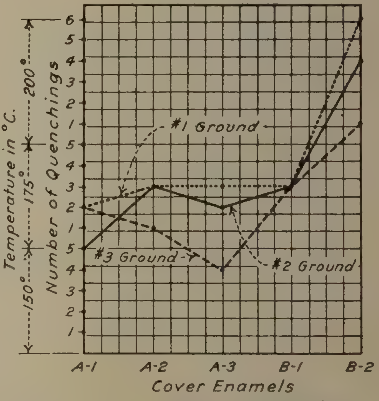

FIG. 5.—The effect of zirconia on resistance of cover coats to thermal shock.

3. Although the resistance to thermal shock of the zirconia enamels is higher than the tin enamels, increasing amounts of zirconia in the smelter batch decreases the resistance. Increased substitutions of zirconia for tin oxide in the mill increases the resistance to thermal shock.

4. Additions of zirconia to the smelter batch did not increase the

resistance to attack by acid. Substitution of zirconia for tin oxide in the mill did show a beneficial action by slightly increasing the resistance.

5. Zirconium oxide can be used as a satisfactory substitute opacifier for tin oxide in the mill additions.

6. Summary

The use of zirconia in kitchen ware enamels is beneficial in its effect upon the essential properties of the enamel. It was found that the resistance to acid was increased in agreement with the statement of Staley.[1] The enamels were made stronger and more resistant to thermal shock here confirming the investigation of Fritz Kraze.[2] It was also found in accordance with Wenning's[3] conclusions that zirconia makes a more viscous enamel, gives a good white body with opacity as good as tin oxide.

The results on opacity do not agree with those of Morgan and Charles, Jr., that zirconia could not be used as a substitute opacifier for tin. This disagreement may be due to two causes; first, they give no statement as to the source of the zirconia used, and may have had an inferior grade; second, the composition of the white used is not in agreement with the base white of this investigation. The white base used by Morgan and Charles, Jr., was a high fluoride enamel while the base white used in the work was an antimony enamel high in cryolite, also containing zinc oxide.

A further field of investigation could be suggested in which the compositions of the enamel and combinations of ground and cover coats could be worked out to give very satisfactory results.

The writer wishes to extend his hearty appreciation and thanks to the Coonley Manufacturing Company for the samples of ware, also to Dr. Miner of the Welsbach Company for the zirconia used in the above investigation, and to R. R. Danielson and C. W. Parmelee for the many helpful suggestions toward the completion of this work.

Ceramic Department
University of Illinois
June, 1923

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[1] Staley, *loc. cit*

[2] Kraze, *loc. cit.*

[3] Wenning, *loc. cit.*

THE MICROSCOPIC IDENTIFICATION OF STONES IN GLASS[1]

By Herbert Insley

ABSTRACT

For the identification of stones in glass, it is not only necessary to observe the external form of the crystalline substances forming the stones, but also to determine their optical properties by means of the polarizing microscope.

A brief description of the method of preparation of stones for microscopic examination is given.

The principal optical properties and distinguishing characteristics of the crystalline substances occurring in stones in the soda-lime glasses are noted.

Introduction

Bowen[2] has pointed out that, because of their crystalline nature, stones in glass may be readily identified by means of the polarizing microscope. He has also shown that the source of the stone is indicated by the composition and structure of the crystals, and he has given the optical properties of the stones found in optical glass. In a recent paper, the writer[3] has shown that the stones occurring in tank glasses, although in part of different compositions from those found in pot glasses, can also be identified and traced to their sources by the use of the polarizing microscope.

The impression seems to have been left with glass technologists that stones could be identified by their external form alone. Many crystalline compounds have widely differing compositions, although very similar in external form, and it is, therefore, necessary to determine the optical properties before satisfactory identification can be made. The object of the present paper is to note the methods of examination and to give the distinguishing properties of the crystalline compounds occurring in the soda-lime glasses.

A knowledge of the composition of stones in glass should enable the plant technologist to eliminate them since he already has information on the batch composition, the temperature conditions in the tank and the condition of the tank walls. The polarizing microscope affords him a means of determining the composition of the crystalline parts of the stones which is more exact and more rapid than that of chemical analysis. A working knowledge of the methods of determining the optical properties of crystalline materials is, of course, essential to the efficient use of the polarizing microscope.[4]

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[1] Published by permission of the Director of the Bureau of Standards of the U. S. Department of Commerce.

[2] N. L. Bowen, "The Identification of Stones in Glass," *Jour. Amer. Ceram. Soc.*, **1**, 594–605 (1918).

[3] *Jour. Amer. Ceram. Soc.*, **6** [6], 706–16 (1923).

[4] The following books are of great assistance in understanding the theory of optical crystallography as well as the methods of optical measurement with the microscope: Albert Johannsen, "Manual of Petrographic Methods." Second edition. McGraw-Hill Book Co., 1918. (A complete discussion of theory as well as a compilation of

One of the most important properties to be determined is the index of refraction. To make this determination, it is necessary to crush the specimen to a powder and immerse in liquids of known index of refraction. Before crushing, the stone should be freed from the surrounding glass as much as possible. This can be done by breaking the glass containing the stone into fragments one-sixteenth to one-thirty-second of an inch in diameter and separating the stony material from the clear glass by means of a probe under the binocular microscope. All of the optical properties may be determined by the use of the immersion method, but for the preservation of typical stones and for the observation of structure, thin sections are very valuable.

The source of the stone is sometimes indicated by its manner of occurrence. Stones derived from the tank walls are frequently accompanied by lumps in the finished glass. Grains of undissolved sand may be altered wholly or in part to the high temperature modifications of silica and may frequently be surrounded by devitrification crystals of tridymite. Other undissolved batch constituents also may be surrounded by aureoles of devitrified glass, the crystals in the devitrified area having a chemical composition closely related to that of the undissolved batch constituent. Devitrification crystals frequently occur as radiating spherulites or feathery aggregates.

A list of the crystalline compounds occurring in the soda-lime glasses is given below. The optical properties of each compound, the usual habit of the crystals, their associations, the different types of stones in which they occur, and the properties most useful for distinguishing them from other crystalline materials in glass are also noted.

Quartz.—(SiO_2)—Stable below 870°C. Usually occurs as grains with rounded and sometimes embayed faces. Crystals with well developed faces are seldom, if ever, seen in stones. Its indices of refraction are: $\omega = 1.544$, $\epsilon = 1.553$, and it is uniaxial positive in optical character. It has no recognizable cleavage. Its characteristic properties are its indices of refraction, its double refraction, the shape of the grains and its associations. Quartz has never been observed as a crystallization product of the glass and is only found in either batch or tank stones (stones derived from the refractory walls of the tank). In batch stones it is sometimes the only crystalline material, but more usually it is associated with tridymite

methods); Esper S. Larsen, "The Microscopic Determination of the Nonopaque Minerals," U. S. Geol. Surv., *Bull.* **679** (1921). (Gives a discussion of the immersion method as an introduction to a list of the optical properties of the known minerals); N. H. and A. N. Winchell, "Elements of Optical Mineralogy." 2d ed., Pt 1. D. Van Nostrand and Co., 1922. (A concise discussion of theory as well as of modern practice); F. E. Wright, "The Methods of Petrographic-Microscopic Research." Carnegie Inst. Washington, *Pub.* **158** (1911). (A discussion of the accuracy and limitations of the methods of optical mineralogy).

and cristobalite. In tank stones it is associated with dehydrated clay substance, sillimanite, etc.

Tridymite.—(SiO_2)—Stable between 870° and 1470°C. Tridymite may occur in hexagonal plates or wedge-shaped and interpenetration twins, depending on the mode of formation. Devitrification crystals are usually simple hexagonal plates, crystals resulting from the inversion of quartz grains are usually twinned. The indices of refraction are $\alpha = 1.469$, $\beta = 1.470$, $\gamma = 1.473$. The optical character is biaxial positive and the acute bisectrix is normal to the hexagonal plate. The crystals are probably orthorhombic. The hexagonal plates are most frequently seen turned on edge when they appear as needles or laths with parallel extinction and negative elongation (elongation $= \alpha$). Plates arranged in parallel layers are abundant.

Tridymite occurs in batch stones where the undissolved constituent is quartz, in devitrification stones, in crown drops and frequently in the scum on the melting surface of tanks. In batch stones it occurs either as hexagonal plates or wedge-shaped twins and is usually associated with quartz and sometimes with cristobalite. The large white spheres so frequently found in devitrified glass sometimes contain hexagonal plates of tridymite arranged irregularly with respect to each other and in a matrix of glass. Under the microscope the plates appear as needles or laths. Tridymite appears as large wedge-shaped or more intricate twins in crown drops and simple hexagonal plates are rarely seen. In scums on the melting surface where the crystallizing constituent is silica, tridymite usually forms the uppermost part of the scum, cristobalite forms the lower layer of the scum and there is a gradual transition between the layer predominantly cristobalite and the layer predominantly tridymite. Tridymite in scums may appear as hexagonal plates, wedge-shaped twins or both. The distinguishing properties of tridymite are the indices of refraction, the character of the elongation of the upturned hexagonal plates, the wedge-shaped twins and the crystalline materials with which it is associated.

Cristobalite.—(SiO_2)—Although cristobalite's stability range is from 1470°C to its melting point, it appears at temperatures which are considerably less than 1470°. It very often is the intermediate crystalline form of silica in the inversion of quartz to tridymite and it sometimes crystallizes directly from the melt at temperatures below 1470°. Cristobalite most frequently appears as very small skeleton crystals[1] arranged in parallel growths. Complete crystals have never been observed in glass by the writer. The indices of refraction of cristobalite are about 1.484 and 1.487 and the double refraction is very low. Cristobalite occurs in batch stones associated with tridymite and undissolved quartz grains, in scums on the melting surface associated with tridymite, and in devitrification crystals. In devitrification crystals the pine-tree growths are characteristic.[1] Cristobalite is readily identified by its index of refraction and characteristic skeleton crystals and parallel growths.

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[1] Fenner, *Amer. Jour. Science*, **36** [4], 355 (1916).

Wollastonite.—($CaO.SiO_2$)—Wollastonite is monoclinic with its elongation parallel to the crystallographic b axis and consequently it appears to have parallel extinction. It occurs in laths or needles. Since the vibration direction β is parallel to the elongation, the elongation may be positive or negative, but due to the fact that the index of refraction β is very much closer to γ than it is to α, the elongation usually appears positive. The indices of refraction are $\alpha = 1.616$, $\beta = 1.629$, $\gamma = 1.631$. The optical character is biaxial negative. Wollastonite occurs only as a devitrification product and usually as radiating feathery or spherulitic aggregates. Wollastonite may be distinguished from sillimanite by its slightly lower indices of refraction, its habit and the fact that the laths are somewhat broader than the sillimanite needles. It may be distinguished from diopside by its lower indices of refraction and its parallel extinction.

Diopside.—($CaO.MgO.2SiO_2$)—Diopside has been observed in two instances by the writer, once as a devitrification spherulite and once as the crystalline constituent of the scum on the melting surface of a tank. In both cases the limestone used in the batch was dolomitic. Diopside can evidently only occur as a devitrification product where magnesian limestone or some magnesia compound is used in the batch.

Diopside occurs in slender prismatic crystals with a maximum extinction angle of about 40°C. The indices of refraction are $\alpha = 1.673$, $\beta = 1.680$, and $\gamma = 1.702$.[2] It is biaxial positive in optical character. Diopside is easily distinguished from other crystalline compounds in glass by its indices of refraction and its extinction angle.

Sodium-Calcium Silicate.—The exact formula of this compound is not known. It occurs in slender crystals as a devitrification product. The prismatic crystals have a hexagonal or octagonal cross-section. The indices of refraction are: $\alpha = 1.562$, $\gamma = 1.577$[3] and the optical character is biaxial positive. The extinction is parallel and the elongation is positive ($= \gamma$). The indices of refraction, habit, and character of elongation are sufficient to distinguish this material from other crystals occurring in glass.

Sillimanite.—($Al_2O_3.SiO_2$)—Sillimanite is found only in stones derived from the pot or tank walls. It occurs in orthorhombic needles and slender laths which have a characteristic appearance. Its indices of refraction are: $\alpha = 1.638$, $\beta = 1.642$, $\gamma = 1.653$. Sillimanite has parallel extinction and

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[1] *Jour. Amer. Ceram. Soc.*, **6**, 708 (1923).

[2] The indices given were determined on crystals occurring in a scum on the melting surface of a tank. They are somewhat higher than those given for pure artificial diopside by Wright and Larsen, *Am. Jour. Sci.*, **27**, 1 (1909).

[3] Indices were determined by the writer.

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positive elongation (= γ). It is very frequently associated with dehydrated clay that has not dissolved in the glass or transformed to sillimanite and is sometimes associated with quartz grains or corundum crystals. Sillimanite can be identified by its indices of refraction, crystal habit, extinction and character of elongation.

Corundum.—(Al_2O_3)—Stones containing corundum have, without doubt, been derived from the refractory walls of the pot or tank. Corundum crystals, as they occur in glass, are very thin, hexagonal plates. The indices of refraction are: $\omega = 1.768$, $\epsilon = 1.760$ and the optical character is uniaxial negative. The double refraction is so low and the plates are usually so thin that interference figures are very faint. The hexagonal plates turned on edge appear as very fine needles with positive elongation. Corundum crystals, which are small (0.002–0.08 mm.) have rounded edges and are associated with clouds of fine-grained amorphous particles, have probably been derived from refractory material below the glass line which contained a high percentage of alumina. Larger corundum plates (0.1–2.0 mm.) which have well defined edges and are not associated with fine-grained amorphous particles have been produced by the action of the soda in the furnace atmosphere upon flux blocks above the glass line. The index of refraction and the crystal form of corundum are usually sufficient to distinguish it from other materials occurring in stones.

Nephelite.—($Na_2O.Al_2O_3.2SiO_2$)—Nephelite has been frequently found by the writer in flux blocks above the glass line which has been exposed to the soda in the furnace atmosphere, but it has been found in a stone in glass in only one case. Here it was associated with corundum and was evidently formed by the action of the molten glass on the corundum under unusual conditions. In thin section the nephelite crystals had a hexagonal cross-section and showed a faint but unmistakable uniaxial negative interference figure. The double refraction was very low, and the index of refraction was slightly less than that of Canada balsam (about 1.54).

Amorphous Substances.—Pot or tank stones very often contain what appear to be opaque masses under low power, but are in reality clouds of very fine, apparently amorphous particles which have resulted from the dehydration and dissociation of the clay minerals. Identification of such masses would be very difficult except that they are almost always associated with masses of sillimanite needles and with rounded and partially dissolved quartz grains.

When salt cake or calcined alumina is used in the glass batch, large stones containing balls of these undissolved materials are sometimes formed. Since the particles making up such stones are very fine and amorphous, identification by means of the microscope is impossible and it is necessary to resort to chemical analysis. Fortunately, stones of this type are usually large and are easily separated from the surrounding glass.

STUDIES ON THE THERMAL CONDUCTIVITIES OF SOME REFRACTORY MATERIALS[1]

ABSTRACT

The method used was a modification of that described by Hepplewhite. The changes made were for the purpose of insuring greater accuracy. An effective means for preventing lateral flow of heat was devised. The coefficients obtained for the several materials studied were (c. g. s. units) silica brick .00099, fire clay brick .00169, fire clay slab .00203, light weight fire clay brick .00251, sillimanite brick .00432, electrically sintered magnesia brick .00655, "Alundum" fire brick .00833, "Crystolon" silicon carbide brick .00982.

[The work for this paper including the design, erection and operation of the apparatus, most of the calculations and the preparation of the detailed report was done by O. S. Buckner.]

Object

These studies were made for the purpose of obtaining reliable conductivity coefficients on several types of refractory bricks made from ceramic bonded electric furnace products. Intelligent use of a new refractory material cannot be made without accurate data. Engineers engaged in furnace design must necessarily know the coefficients of the refractories they are working with in order to determine properly wall thicknesses and to provide for suitable insulation.

Method of Test

The method used in these tests was a modification suggested by Hepplewhite.[2] Hepplewhite devised his method to determine the conductivity of silica refractories at high temperatures. A relatively short temperature gradient through the test piece was used, 1350 to 850°C. The thickness of the test piece was 3 inches.

In order to adapt this method to refractories having a high relative conductivity like fused alumina and silicon carbide the size of the test piece was reduced in area to a circular piece $8^1/_2$ inches in diameter. Care was taken to prevent diffusion of furnace gases into the test piece by protection of the lower surface with a dense refractory plate. An additional air calorimeter or guard ring was placed around the calorimeter on which measurements were taken in order to maintain the entire upper surface at an even temperature. These precautions were not taken by Hepplewhite and it would seem that the result he has obtained on bonded silica is too high. That is, furnace gases are likely to seep through the test piece carrying heat with them to the upper surface of the test piece. Further, failure to maintain the upper surface at an even temperature would

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[1] A contribution from the Research Laboratories of the Norton Co., Worcester, Mass. Received November 9, 1923.

[2] *Bull. Amer. Ceram. Soc.*, **1** [Feb. 20], 5 (1922).

result in lateral flow and this lateral flow, in the case of Hepplewhite's method, would be toward and into the calorimeter.

Below is given a sketch of the apparatus used in these tests (Fig. 1) and a photograph of the set-up (Fig. 2).

Description of Apparatus

Furnace.—The furnace used was a 2-burner gas-fired pot furnace approximately 16 inches in diameter on the inside and 10 inches deep. A 9 x 5 inch round "Crystolon" refractory block was placed in the center of the chamber as a heat retainer. The top was covered with two 29-inch diameter semi-circular fire clay slabs, 3 inches thick, through which at the center was cut an 8-inch round hole. Midway between the burners and at the outside edge of these slabs two diametrically opposite vents were cut for the exit of burned gases. Over the 8-inch hole the test specimen was placed. This was $8^1/_2$ inches in diameter and in most cases 2 inches thick. The lower side was protected from direct contact with the gas flames by a "Crystolon" refractory plate $^3/_8$ inch thick. Between this plate and the test specimen was also $^1/_4$-inch RA 162 "Alundum" cement. This plate and cement also held the platinum platinum-rhodium thermocouples in place. These latter were in the plane of the lower surface and extended $2^1/_2$ inches from the outside circumference toward the center of the specimen. They were placed diametrically opposite. The only protection provided for the wires of the couples was "Alundum" insulation tubing and about $^1/_4$-inch pure 38 "Alundum" abrasive packed around the end of the couple itself. The lower surface had to be grooved about $^1/_8$ inch deep to permit the couple wires being placed in the plane of the lower surface. Three base metal couples were used to measure the temperature of the upper surface. These were placed parallel to one another in grooves about $^1/_8$ inch deep, $2^1/_2$ inches apart. The couple joints themselves were all on one diameter of the upper surface. No insulation was necessary

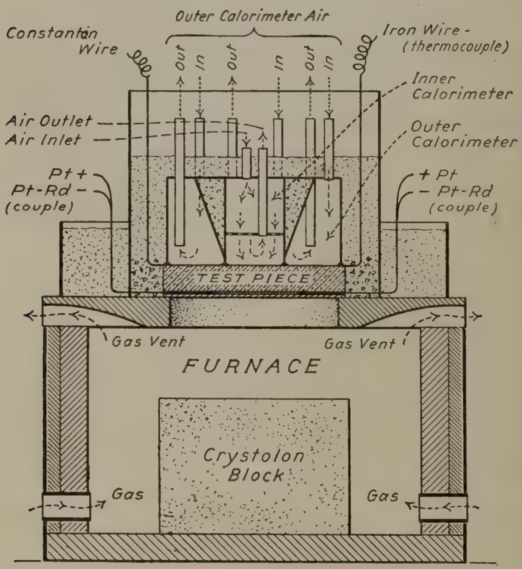

FIG. 1.—Construction and arrangement of the calorimeters.

since the positive and negative wires were in one straight line. The grooves in which the wires were placed were filled up with a mixture similar in composition to the block being tested, the wires and couple joint being covered to a depth of $^1/_{16}$ inch.

The calorimeter was made of thin sheet iron and was 4 inches in diameter and 6 inches high. Air was blown into the top of this calorimeter at the center, broken up and distributed over the top of the specimen below by means of a perforated plate 2 inches above the specimen. The air came into direct contact with the specimen and passed out through the top by means of a $^1/_2$-inch pipe opening below the perforated plate. The temperatures just above the calorimeter of the ingoing and outgoing air were measured with mercury thermometers. An outer calorimeter or guard ring was employed to keep the remainder of the top surface of the specimen at the same temperature as that portion covered by the inner calorimeter. This outer calorimeter touched, but was not joined to, the inner calorimeter, $^1/_4$ inch above the surface of the test piece. Except at this point they were separated with powdered kieselguhr tightly packed in between them. The bottoms of the calorimeters were sealed to the top of the test specimen with RA 162 "Alundum" cement, a thin layer being applied to each in the same manner as putty is used on window glass. This cement was also coated over with a thick solution of silicate of soda. There were five openings and five exits for air evenly spaced about the top of the outer calorimeter. The lower ends of these pipes were flush with the top of the calorimeter in the case of the former and one inch above the surface of the specimen in case of the latter.

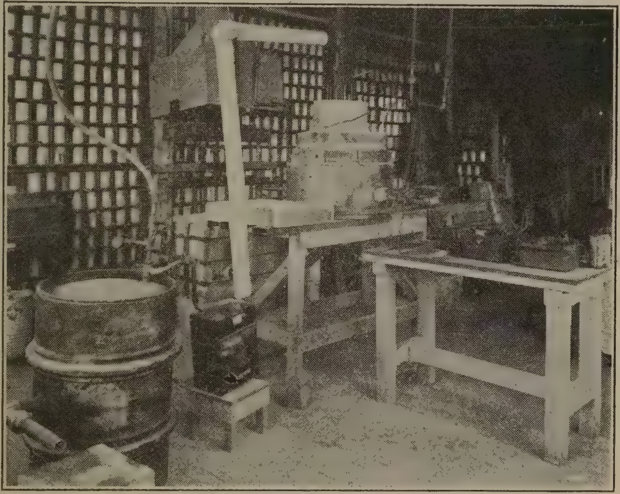

FIG. 2.—Set-up of the apparatus.

A 15-inch diameter galvanized iron hoop was placed around the test piece and calorimeter, and the test piece and calorimeter were protected from loss of heat by tightly packed kieselguhr with which the hoop was filled to a point about $1^1/_2$ inches above the calorimeters. To a point slightly above the test piece, quartz was added to the kieselguhr to reduce the shrinkage in this material.

Air was furnished the calorimeter by means of a small electric blower and the volume delivered to the inner calorimeter was measured by means of an 8-lamp gas meter. The pressure and temperature of the air was also measured at the meter. A small steel tank was interposed between the blower and the motor to thoroughly mix the air, for it became slightly heated in passing through the blower. Connection was made from the tank to both outside and inside calorimeters by $^1/_2$-inch steel pipe and rubber tubing.

The noble metal couples on the bottom surface of the test specimen were calibrated after every two runs. They varied very little throughout the study except in the test of the "Crystolon" refractory. In this case it was found necessary to protect the thermocouple wires with "Alundum" tubing which had been rendered impervious by a glaze of porcelainic composition. The hot junction of the couple was similarly protected by packing it in "Alundum" cement and then painting a raw porcelainic glaze over the cement. Silicon fumes probably were the cause of the trouble. Due to oxidation the base metal couples had to be replaced three or four times.

The accuracy of the gas meter used was not known. However, it had just been calibrated before being borrowed from the Worcester Gas Light Company. In a talk which Mr. Buckner had with Mr. Bauer of the Providence Gas Company he was told that gas meters were very accurate measuring devices; that of 20,000 meters used in Providence in 1920, the maximum error found in this number after one year's use was 2%.

Composition of Test Pieces

The pressed fire clay mixture consisted of $12^1/_2$% sandy and $37^1/_2$% of plastic fire clay with 50% by volume of 3- to 16-mesh fire clay grog. The grog was reclaimed from broken slabs and saggers. The light weight refractory had a bulk specific gravity of 1.7. The weight of the standard 9-inch brick was 5.1 lbs. Its composition was plastic fire clay 40%, lignitic clay 40%, 3- to 16-mesh grog 10%, and 16 F grog 10%. These were fired to cone 13.

The sillimanite, electrically sintered magnesia, fused crystalline alumina and silicon carbide refractories were made by crushing the electric furnace products to pass a No. 14 screen and bonding with fire clay. The sillimanite contained 15% of bond, the fused alumina and silicon carbide 10%, and the magnesia 3%. These were fired to cone 16.

Two brands of commercial refractories were also tested, a silica brick composition and a Pennsylvania fire clay composition.

The average chemical compositions of the materials are as follows:

	"Alundum" fused alumina	"Crystolon" silicon carbide	Sillimanite	Electrically sintered magnesia	Bond clay
SiO_2	1.0 –2.5%	..	35.75%	..	59.55%
Fe_2O_3	0.25–1.0	..	1.92	..	2.31
TiO_2	1.5 –4.0	..	2.60	..	1.33
Na_2O	trace	..	..	..	..
Al_2O_3	92.0–96.0	..	59.73 by diff.	..	25.41
ZrO_2	trace–1.25	..	..	..	..
CaO	0–trace	..	..	..	0.46
MgO	0–trace	..	..	92.0–95.0%	0.33
SiC	..	98.0%	..	..	..
$K_2O + Na_2O$	..	..	..	..	1.01
Loss	..	..	..	..	9.10

	Pressed fire clay mixt.	Light wt. fire clay mixt.
SiO_2	67.11%	66.77%
Fe_2O_3	1.61	1.52
TiO_2	1.30	2.00
Al_2O_3	28.20	28.94
CaO	0.80	trace
MgO	1.60	trace
$K_2O + Na_2O$	0.48	0.95
Loss	0.27	0.18

Porosity of Mixtures

The porosities of the test specimens were calculated from the dry, saturated and suspended weights.

	Porosity
Star silica No. 2	27.7%
Star silica No. 3	..
H. W. fire clay No. 1	..
H. W. fire clay No. 2	..
Pressed fire clay No. 2	24.9
Pressed fire clay No. 3	24.9
Light weight fire clay No. 1	42.5
Light weight fire clay No. 3	41.2

	Porosity	
Sillimanite	15.2	one sample only
Magnesia	23.4	one sample only
"Alundum" fused alumina No. 1	14.3	
"Alundum" fused alumina No. 2	13.6	
"Crystolon" silicon carbide	29.14	

Operation of Apparatus

The temperature of the furnace was slowly raised over a period of 6 to 7 hours in all tests till the temperature of the bottom of the specimen reached 1250°C. When the bottom had reached about 900°C it was found necessary to turn on the blower and admit air to the calorimeters in order to prevent the rubber connections from charring. A strong current was first admitted to the inner calorimeter, and if the seal at the bottom was not tight, air could be felt issuing from the exit pipes on the outer calorimeter. Readings of the three base metal couples on the top surface were made shortly after turning the air into the calorimeters and the supply regulated to give equal temperatures at the three points. The top surface gradually rose to 650°C and the supply of air was so regulated as to hold it constant at this point. When the apparatus became thermally balanced the air pressure and the psychrometer were read. The duration of the tests was 20 minutes, and each minute temperature readings were taken of ingoing and outgoing air at the calorimeter. The pressure and temperature of the air at the meter were also read. Knowing the volume of air which passed through the meter in 20 minutes, there were sufficient data to calculate the coefficient of conductivity.

Method of Calculation of Coefficient

The following is a sample calculation. These data were obtained on run No. 2, "Star" silica.

Barometric pressure, 743.45 (corrected)
Average temp. of air at meter, 34.1°C
Manometer at meter, 0 mm.
Volume of air used, 8.8 cu. ft.
Vapor pressure, 14.27 mm. (obtained from psychrometer readings. See Psychrometric Tables W. B. No 235, U S. Dept. of Agr.).
Average temperature of ingoing air at calorimeter, 42.58°C
Average temperature of outgoing air at calorimeter, 232.29°C
Thickness of block, 4.121 cm.
Area of calorimeter, 80.58 sq. cm.
Temperature of lower surface of test piece, 1250°C
Temperature of upper surface of test piece, 650°C
Duration of test, 1200 sec.
Specific heat of H_2O vapor, .468 (Smithsonian tables)
Specific heat of air, .237
Weight in gms. of 1 cu. ft. dry air, 36.61
Weight in gms. of 1 cu. ft. H_2O vapor, 22.775

Since the volume of a gas is directly proportional to the absolute temperature and inversely proportional to the pressure, the volume of air used calculated to standard conditions becomes:

$$\frac{8.8}{V} = \frac{307.1 \times 760}{273 \times 743.45}$$
$$V = 7.65 \text{ cu. ft.}$$

As used, this air contained sufficient moisture to give a vapor pressure of 14.27 mm. The volume of water vapor present bears the same relation to the volume of air as the vapor pressure does to the total pressure.

$$7.65 \text{ cu. ft.} \times \frac{14.27}{743.45} = .146 \text{ cu. ft. } H_2O \text{ vapor}$$
$$7.65 - .146 = 7.504 \text{ cu. ft. dry air.}$$

The amount of heat carried out of the calorimeter by these two gases is equal to their respective weights multiplied by the rise in temperature and their specific heats, or

7.504 × 36.61 = 274.72 gms. of dry air
274.72 × (232.29° − 42.58°) × .237 = 12,351.76 calories
.146 (H_2O vapor) × 22.775 = 3.325 gms. H_2O
3.325 × (232.29° − 42.58°) × .468 = 295.20 calories
12,351.76 + 295.20 = 12,646.96, total calories taken from calorimeter.
The coefficient of conductivity =

$$\frac{\text{Heat} \times \text{thickness}}{\text{Area of calorimeter} \times \text{temp. difference of sides} \times \text{time in sec.}}$$

Therefore,

$$K = \frac{12{,}646.96 \times 4.070}{80.58 \times 600 \times 1200} = .00089.$$

The area of the calorimeter used here was obtained by moistening the lower edge of the calorimeter with ink, making several imprints on paper and taking the area of these circles with a planimeter. The outside area was used in the calculation since the metal of the calorimeter absorbed heat from the block and gave it up again to the calorimeter air.

The "thickness of block" used in the calculations above is the thickness of the test specimen minus $^1/_{16}$ inch or the actual distance between the thermocouples on the bottom and upper sides of the test piece.

Data

TABLE I[1]

	Silica No. 2	Silica No. 3	H. W. fire clay No. 1	H. W. fire clay No 2.
Barometric pressure	743.45 mm. Hg	744.0	746.7	744.8
Volume air used	8.8 cu. ft.	6.67	11.07	13.32
Vapor pressure	14.27 mm.	5.56	7.0	12.85
Air at meter	34.1°C	27.3	30.85	42.77
Manometer	0.0	..	..	..
Calorimeter air (in)	42.58°C	39.7	40.76	50.65
Calorimeter air (out)	232.29°C	288.19	304.0	297.54
Thickness of test piece	1.665″	2.02	1.728	1.71
Temperature of bottom	1250°C	1250	1250	1250
Temperature of top	650°C	650	650	650

	Pressed fire clay No. 2	Pressed fire clay No. 3	Light weight fire clay No. 1	Light weight fire clay No. 3
Barometric pressure	740.0 mm. Hg	745.8	744.0	745.8
Volume air used	16.70 cu. ft.	12.60	15.79	15.96
Vapor pressure	21.3 mm.	16.20	12.5	14.9
Air at meter	40.3°C	39.5	36.0	36.6
Manometer	..	..	..	..
Calorimeter air (in)	45.0°C	50.11	43.2	47.94
Calorimeter air (out)	251.0°C	280.68	314.5	280.03
Thickness of test piece	2.04″	2.04	1.97	1.97
Temperature of bottom	1250°C	1250	1250	1250
Temperature of top	650°C	650	650	650

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[1] The values given for temperature are averages.

	Sillimanite No. 3	Sillimanite No. 4	Magnesia No. 1	Magnesia No. 2
Barometric pressure	748.21 mm. Hg	747.7	744.0	741.3
Volume air used	34.95 cu. ft.	34.37	50.22	47.9
Vapor pressure	17.45 mm.	17.06	15.87	0.24
Air at meter	42.88°C	46.05	28.7	29.0
Manometer	1.0 mm.	1.0	2.0	2.0
Calorimeter air (in)	53.86°C	56.2	35.3	34.4
Calorimeter air (out)	252.0°C	245.76	239.0	242.4
Thickness of test piece	2.053″	2.053	1.983	1.983
Temperature of bottom	1250°C	1250	1250	1250
Temperature of top	650°C	650	650	650

	"Alundum" fused alumina No. 1	"Alundum" fused alumina No. 2	"Crystolon" silicon carbide
Barometric pressure	752.8 mm. Hg	736.7	749.6
Volume air used	50.5 cu. ft.	46.8	23.1
Vapor pressure	8.81 mm.	9.32	5.08
Air at meter	33.47°C	32.64	28.6
Manometer	4.0 mm.	4.0	3.0
Calorimeter air (in)	35.46°C	38.42	39.03
Calorimeter air (out)	242.42°C	245.9	313.48
Thickness of test piece	2.54″	2.53	3.54
Temperature of bottom	1250°C	1250	1188
Temperature of top	650°C	650	730

Results

TABLE II

	Coefficient of thermal conductivity (c. g. s. units)	
	Determined	Average
Silica No. 2	0.00089	
Silica No. 3	.00109	0.00099
H. W. fire clay No. 1	.00163	
H. W. fire clay No. 2	.00175	.00169
Pressed fire clay No. 2	.00220	
Pressed fire clay No. 3	.00187	.00203
Light weight fire clay No. 1	.00269	
Light weight fire clay No. 2	.00233	.00251
Sillimanite No. 3	.00448	
Sillimanite No. 4	.00417	.00432
Magnesia No. 1	.00667	
Magnesia No. 2	.00643	.00655
"Alundum" fused alumina No. 1	.00873	
"Alundum" fused alumina No. 2	.00793	.00833
"Crystolon" silicon carbide No. 1	.00982	.00982

For the purpose of comparison there are given below results obtained by others on refractories at high temperatures:

TABLE III[1]

	Temp. interval	Coefficient (c. g. s. units)
Silica	165–1015 °C	0.0033 burned at 1300 °C
Magnesite	185–915	.0060 burned at 1300
Fire brick	310–1000	.0054 burned at 1300
Glass pot mixture	175–1150	.0029 burned at 1200
Carborundum	420–1000	.0150 burned at 1300

TABLE IV[2]

Silica	0.0020	Temp. interval and temp. of burning unknown.
Fire brick	.0034	
Magnesite	.0071	
Carbofrax	.0243	

TABLE V[3]

	Mean temp.	Coefficient
"Alundum" fused alumina	900 °C	0.0068
Sillimanite	900	.0044
"Crystolon" silicon carbide	900	.0235

TABLE VI[4]

	Temp. interval	Coefficient
Silica	700–800 °C	0.0035[4]
Magnesite	100–900	.0081[4]
Silica	550–1440	.0040[5]
Magnesite	690–1370	.0091[5]
Silica	850–1350	.00105[6]

Discussion of Results

The relative order of the conductivities of the refractories studied, referred to the pressed fire clay mixtures is, pressed fire clay 1.0; sillimanite 2.1; magnesia 3.2; fused alumina 4.1; silicon carbide 4.8.

The most marked differences between these results and those obtained by others are to be found for silica and fire clay. The average result for silica, 0.00099, is but one-third as much as obtained by Wologdine, and Goerens and Gilles, one-fourth as much as obtained by Doughill, Hodsman and Cobb, and one-half as much as obtained by Linbarger. Similarly, the results for fire brick are noticeably lower. Hepplewhite using an air calorimeter obtained a result, however, which is not so markedly different from that obtained by this laboratory. Hepplewhite, finding his results lower than those of others apparently sought only for a reason to explain this discrepancy. The construction of his calorimeter, lateral flow through the test specimen and permeability of the latter to hot gases, as before mentioned, appear to be of more importance than the source of error he has mentioned and these would increase, not decrease his result.

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[1] Wologdine, *Electrochem. & Met.*, **7**, 383 (1909).

[2] Linbarger, *Chem. & Met. Eng.*, **19**, 489 (1919).

[3] K. T. Moores, "Thermal Conductivity of Refractories at High Temperatures," M. I. T. Thesis, Norton Library.

[4] Goerens and Gilles, *Ferrum*, **12**, 1–11, 17–21 (1914).

[5] Doughill, Hodsman and Cobb, *Jour. Soc. Chem. Ind.*, **34**, 468 (1915).

[6] Hepplewhite, *loc. cit.*

The result obtained for sillimanite is practically identical with that obtained by Moores. However, his result for "Alundum" is considerably lower and that for "Crystolon" higher. Moores' test specimens were burned at cone 12.

No attempt was made to determine the effect of the temperature of burning, the porosity and permeability on the conductivity of refractories. Wologdine in this connection found the conductivity of fire clay, bauxite, and silica refractories to increase materially with temperature of burning. Increasing the porosity of fire clay reduced the conductivity, while increasing the permeability increased the conductivity.

Wologdine further found that the conductivity of fire clay, silica and bauxite increased with temperature, although the increase was small. Moores on the other hand found the coefficient to decrease in the case of "Alundum," "Crystolon" and sillimanite. It would seem that one or the other must be wrong.

A complete check was not obtained upon "Crystolon" silicon carbide. Owing to the failure of the furnace air compressor a few minutes after starting the test, complete data were not obtained. However, those obtained are in fair agreement with the data reported by others.

THE FIRING OF REFRACTORY PRODUCTS IN FRANCE[1]

By R. V. Widemann

ABSTRACT

Importance of the question for a country where fuel is expensive and resources are less than consumption.

Types of Kilns Used.—Principally continuous kilns; some intermittent ones and a few tunnel kilns.

Heating of Kilns.—Heating direct or with gas—evolution of ideas.

Conclusion.—Heating in modern kilns consists in transporting calories from one point to another with the minimum of loss, the hearth serves only to compensate these losses while raising the calories to a higher potential.

The firing of refractory products can be considered either from the purely technical point of view of the influence of the firing temperature on the quality of final product, or from the economic point of view of obtaining this firing temperature in the least onerous manner.

The fuel question plays an important part in the ceramic industry, particularly in the making of refractories; it is one of the important elements in cost of production, especially in a country like France in the present situation.

Our[2] production of coal in 1913 amounted, in round numbers, to 40 million tons; in 1921 due to our coal mines having been destroyed, the extraction was only 28 million tons. In 1920, although our needs amounted to 80 million tons, we were able to obtain, both in French and foreign coals, not more than 50 million tons.

The saving of fuel, undertaken in all of the great nations, presented then and still presents to our country a primordial interest.

The point of these various statements is to show very briefly the technic of firing in the industry of refractory products in France and the evolution of ideas in respect to firing.

Principal Types of Kilns

The kilns used in France are of three sorts: (*a*) intermittent kilns; (*b*) continuous kilns with products stationary and fire moving; (*c*) continuous kilns with products moving and fire stationary.

My general impression, borne out by reading the *Journal of the American Ceramic Society*, is that the continuous furnace is used more in France than in the United States. Our factories are of little importance in comparison but every French factory works with fire moving continuous kilns. The use of kilns of category (*c*) is just beginning to expand, and intermittent kilns are used only for special products.

(*a*) Intermittent kilns.—These in general are rectangular kilns with a capacity varying from 40 to 100 tons; primitively heated with fireplaces and with natural draft. It is not worth while to take up this type of kiln for they present nothing of particular interest. We may mention in passing that the primitive hearth has been replaced by semi-gasifiers; that the mechanical draft tends to replace the draft by chimneys, and that, in order to get the best use of the calories, certain installations have a partial recuperation.

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[1] Read before the Refractories Division, Pittsburgh Meeting, Feb., 1923. Translated from the French by Frederick G. Jackson

[2] France.

This recuperation is brought about in part by enlarging the exit flues to allow the firing of products which do not require a very high temperature and partially by relying on the neighboring kilns to use the heat generated in periods of little firing.

For certain kilns heated with gas, it is even possible to use kilns that are cooling, as recuperators, to heat the air used in the combustion of another kiln.

Continuous Kilns with Products Stationary and Fire Moving.—These generally consist of between sixteen and twenty-four chambers on two parallel lines. The chambers have a capacity of 10 to 20 tons each. Sometimes they are separated by a fixed wall. Sometimes this wall is made of the product to be fired. The uniting of these furnaces into a one-piece body of reinforced concrete gives good results. They make a very flexible plant, each kiln having three to six chambers, and each burning only twenty-four hours. Their operation is more economical as well as easier the more rapidly they are operated.

They are generally heated by one or several gas generators, placed at the end of the kiln, but at certain factories coal is introduced directly through holes in the roof of the kiln. The use of a mechanical method of distributing the coal of the special type as recently described in the *British Clay Worker*[1] or similar types is being built in France.

Continuous Kilns with Products Moving and Fire Stationary.—Although one of the first kilns of this type (Faugeron kiln) has given interesting results, and although these were originated in France, factories using tunnel kilns for refractory products are scarce and all of recent construction.

The characteristics of kilns of this type present nothing of especial interest, having been given very complete publicity in the September, 1922, number of this *Journal*.[2]

Heating of the Kilns

It might be said that the firing of refractory products is a part of the problem of burning in general. In this case it is the most important since these kilns come in the class of high temperature kilns. But if on the other hand lower temperatures do not interest our industries we must not forget that drying plays an important rôle and that in consequence we use low temperatures or, to speak more exactly, great quantities of calories at low potential. The problem of heating ceramic kilns should therefore be considered not only from the point of view of getting the firing temperature most economically, but also of using the maximum amount of the heat now lost.

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[1] No. 367, November, 1922, page 246.

[2] "Preliminary Report of the Committee on Fuel Conservation on the Railroad Tunnel Kiln," *Jour Amer. Ceram. Soc.*, **5** [9], 602 (1923).

In the results published from time to time on kilns one learns in general that firing to a temperature which is not by any means always indicated has been obtained with per cent of a fuel of which perhaps the name is mentioned, but rarely the composition, and less often the calorific value.

In various tests which we have made we can say that in order to fire to cone 13 or 14 the following results expressed in calories per ton of product burned are required.

(*a*) Intermittent kilns.—1,500,000 to 2,500,000 calories according to the dimensions of the furnaces, their age, and the nature of the product fired.

(*b*) Continuous kilns with products stationary with fire moving.—With different methods of heating the number of calories required is from 900,000 to 1,000,000 per ton.

(*c*) Continuous kilns with products moving and fire fixed.—This figure is estimated at 600,000 calories per ton.

Presented in this form these results may at first cause surprise but if you follow this presentation you will see that a continuous kiln of class (*b*) will consume (if there is used the same fuel at 7,000 calories), in heating direct, about 130 kilograms per ton. With gasifiers, about 185 kilograms per ton. This shows the inevitable loss of 25 to 30% due to gasification.

Utilization of Fuel

The economy of fuel being necessary we should look over every possible process of utilization.

A. Direct combustion.
    1. Hand fired grate
    2. Mechanical fired grate
    3. Powdered coal

B. Direct gasification.

C. Preliminary distillation, more or less complete, and utilization of the combustible residue according to (A) or (B).

1. **Hand Fired Grate.**—The hand fired grate is still in use in intermittent furnaces and in the small factories in general. It is about equally used in continuous kilns of class (*b*), but this use, sufficiently common for ordinary products, is rare for refractory products. A conscientious personnel and a close supervision are necessary in order to give good results.

We have had occasion to visit a factory in which the continuous kiln managed by a good burner consumed 8.7% of fuel with hand firing, but a single operator obtained this result and the other kilns of the same system fired 14 to 15% in order to reach the same temperature.

2. **Mechanical Stoking.**—A mechanical stoker as used in boiler

practice and in certain metallurgical furnaces, does not seem to have been applied as yet to the heating of ceramic kilns.

3. **Powdered Coal.**—The producers of refractory wares are hesitating whether rightly or wrongly, about going into the matter of powdering coal on account of the effect that the ashes would have on the ware.

It appears that the idea suggested in the *British Clay Worker* of a direct mechanical distribution of coal in the kiln has a chance of being considered. We know that installations of this nature have been tried in France with a certain success. We realize the advantages of the burning of coal in the very midst of the products to be fired without depending on the handling by workmen. It may be said that in powdered coal lies the possibility of an important simplification of the mechanical installation.

B. Direct gasification.—After having had a great success this system is now losing ground. Actual gasifiers possess a thermic conversion which varies from 70 to 80% and there is a loss of transportation, which cannot be calculated in advance.

In order to use very hot gas it is necessary to have the gasifiers very near the kilns, a thing which is not possible with central batteries of gasifiers, or at least with gasifiers supplying continuous chamber kilns.

In these conditions the actual tendency is to use the gasifiers only when it is desired to have fuel free from elements which might affect the product, or in order to utilize poor fuels impossible to use directly. Studies are being directed to the use in gasifiers of combustibles carrying 50 and 60% of ash.

C. Preliminary distillation.—Distillation, considered from the purely thermic point of view, is also most unjustifiable. This system does not directly interest the ceramic industries, but it should be considered in the interest of general economics, since it makes possible the recovery of by-products. For factories situated in the coal regions the idea of enormous installations for distilling and gasification allows the consideration of the distribution of a poor gas enriched to 1600 to 2000 calories for use in ceramic kilns.

Concluding this brief exposé it is of interest to know that on account of the great dearth of coal in 1920 and the consequent high price of fuel the factories situated in wooded districts have fired their kilns with wood. From results obtained either by firing direct or in gasifiers it is possible to replace one ton of coal by two tons of wood. However, for gasifiers it is advisable to use a mixture of wood and charcoal in equal parts. The use of wood alone would necessitate the altering of the furnaces which were constructed for the gasification of coke or coal.

Conclusions

The firing of refractory products in France is characterized by a large use of continuous kilns with products stationary and fire moving, with a tendency toward mechanical delivery of fuel directly to the very interior of the kiln.

Intermittent kilns are found only in small factories or for firing special products.

The tunnel kiln with products moving and fire fixed is of great interest from an economic point of view. Well constructed and well regulated, it assures an excellent utilization of the calories contained in the products during cooling for the drying operation (an important quantity of calories of low potential) and in part for the firing itself to heat the primary or secondary air to a higher temperature.

The hottest part of the kiln, of relatively small dimensions, may be carefully insulated so as to reduce losses by radiation to a minimum. The weak point of the combustion is that it serves only to recover a part of the calories from the cooling zone at a potential necessary to obtain the firing at the temperature desired for the products under consideration.

The utilization as completely as possible of the calories of the fuel is the goal of every industry. In an appreciation of the value of a kiln should be considered not only the conditions of reaching the proper firing temperature but also the advantages which it presents, of furnishing calories for other operations such as drying or preheating.

We are at this moment in a period of transformation which will doubtless not yet provide the ideal solution from the ceramic point of view but which will represent in every case an improvement and which will contribute very certainly to the progress of the problem of industrial heating in general.

PARIS, FRANCE

HIGH TEMPERATURE LOAD AND FUSION TESTS OF FIRE BRICK FROM THE PACIFIC NORTHWEST IN COMPARISON WITH OTHER WELL-KNOWN FIRE BRICK[1]

By Hewitt Wilson

ABSTRACT

Seventeen samples of fire-clay brick from the Pacific Northwest have been tested with twenty-seven other commercial brands of fire clay, silica, magnesia, chromite, zirconia, diaspore, silicon carbide and crystalline alumina, as well as china clay and crystalline sillimanite products made at the University of Washington. The tests show that the fire-clay brick of the Pacific Northwest vary considerably in quality. According to the high temperature load test, the majority of the local brick are among the upper grades, some are to be classed with the best fire-clay brick and one equal to the best diaspore brick. The brick tested is not the best which can be made from Pacific Northwest materials, for the kaolins in eastern Washington and northwestern Idaho give opportunity for the production of an all-kaolin fire brick.

A method is suggested for testing *super-refractory* materials under load at high temperatures similar to the standard load test for fire clay and silica brick except that the temperatures are measured by cones, and are raised until 10% linear deformation of the brick is obtained. The rate of heating and soaking varies with the brick under test, and the principles learned from the cone fusion test are used in the application of heat. A numerical value, expressing the area under the cone-shrinkage curve, affords an easy method for comparing the high temperature load resistance of various refractories.

The brick which are best able to resist deformation at high temperatures are composed of crystalline materials which have developed a recrystallized bond of the same composition. These are crystalline silica, silicon carbide, corundum and sillimanite, and they resist deformation at temperatures close to their melting points. Amorphous materials like fire clay, diaspore, bauxite or even the very refractory crystalline materials like chromite and periclase, which depend on amorphous silicates for a bond or are contaminated with silicate impurities, will fail with the softening of the bond of the amorphous impurities. The cone fusion of the brick as a whole can not be depended upon to indicate the resistance to load at high temperatures.

Introduction

Although the present Pacific Northwest brick are good, they are not the best that can be made from local materials. They are probably the best that can be made and sold for the present prices, but when the demand comes for a superior article the kaolins of the Inland Empire, in eastern Washington and northwestern Idaho, can be washed and made into brick which will equal any *fire-clay* brick now being manufactured. Four companies are now using the run-of-mine kaolin without washing, their refractoriness being low because of the quartz, mica, and other impurities.

The purification and subsequent changed process of manufacture will not necessitate installation of expensive equipment.[2] Purification by water is slow and requires considerable water, which is not available in large quantities in all parts of the Inland Empire, but for some beds a dry

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[1] Received October 25, 1923.

[2] A. S. Watts, "Mining and Treatment of Feldspar and Kaolin in the Southern Appalachian Region." Bureau of Mines, *Bull.* **53** (1913).

process can undoubtedly be devised, whereby the majority of the impurities can be removed. The long dry spell in the summer time affords opportunity to dry by the "field" system, but the modern filter presses can be used for more rapid work.

A suggested dry process consists of (1) thoroughly drying the clay, (2) a coarse disintegration through toothed or spaced rolls, (3) a fine disintegration in a high-speed, fan-type disintegrator which is now used in pottery and tile plants and followed by (4) air separation of the quartz and coarse mica from the kaolin. Some fine quartz and mica will be carried along with the kaolin. The air separation method is now in use in the diatomaceous earth plants of Washington and is a common method for other materials. Whether the purification is made by water or air, it will be necessary to either calcine part of the kaolin for grog or replace a portion of the quartz to control shrinkage and cracking. In some of the clays white mica is the chief fluxing impurity and very careful flotation is required to separate it from the kaolin.

In all the tests, standard pyrometric cones were used as indicators of heat treatment. For the fusion test the bricks were sampled after the load test.

Before sampling, each brick was cleaned of all adhering matter by grinding on an emery wheel. The samples were ground to pass a 60-mesh sieve, molded with gum and fired with the standard cones in an oxygen-acetylene furnace.[1]

In case the brick had softened considerably in the load test, the cone fusion may be appreciably lower than that of a fresh specimen.

In Fig. 1, the two full heavy lines represent the maximum and minimum pyrometer readings obtained for the respective cones in the load test kiln. The dotted lines join Brown and Murray's results for fast heating of cone 9[2] to Kanolt's data[3] beginning at cone 26. The small circles beginning at cone 26 show the temperatures found for cones 26 to 38 fired in the oxygen-acetylene cone fusion furnace. With the exception of those below cone 30, they compare very well with Kanolt's figures.

High Temperature Load Tests

The present test for siliceous fire-clay brick under load at high temperatures, proposed by the American Society for Testing Materials,[4] consists of heating the standard nine-inch brick, standing on end and loaded to 25 pounds per square inch, to 1350°C in four and one-half hours. After holding this temperature for one and one-half hours, the furnace is cooled and the brick measured for contraction. The brick shall not show a contraction of more than 4% of the original length. Silica brick are carried to 1500°C in a similar manner.

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[1] Hewitt Wilson, "An Oxygen-Acetylene High Temperature Furnace," *Jour. Amer. Ceram. Soc.*, **4**, 835 (1921).

[2] G. H. Brown, and G. A. Murray, "Function of Time in the Vitrification of Clays," *Trans. Amer. Ceram. Soc.*, **15**, 213 (1913).

[3] C. W. Kanolt, U. S. Bur. Stand., *Tech. Paper* **7**, 15 (1911).

[4] Standard test for refractory materials under load at high temperatures, "designation," C 16, adopted by the A. S. T. M. in 1920. See *Year Book*, Amer. Ceram. Soc., 36, 37, 47–51 (1921–22).

Many of the present higher grade refractories will easily stand this test, and, therefore, it does not clearly distinguish between their relative softening behaviors. 1350°C is far too low a temperature for testing super-refractories used in service above 1600°C. Increasing the load to cause failure at 1350°C also will not indicate the behavior of the brick under light loads at 1600°C. For service at 1600°C, the brick should be heated to 1600°C or higher, under the same or slightly higher loads than those to which they will be subjected in service.

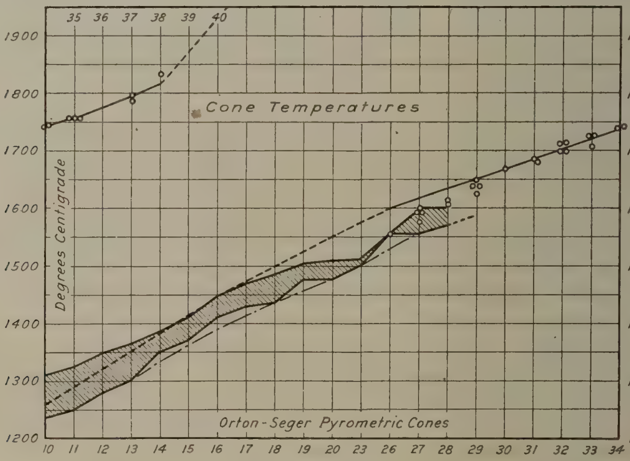

FIG. 1.

The method used for this investigation consisted of heating the brick, standing on end and subjected to a load of 25 pounds per square inch to an increasing temperature, until a contraction of 10% was reached. The expansion and following contraction were measured by a screw gage attached to the leveling mechanism of the loading beams. The furnace is very similar to that suggested by the American Society for Testing Materials. The temperatures were measured by both pyrometric cones and a new Leeds and Northrup optical pyrometer. As soon as the brick started to shrink, the temperature was held until most of the shrinkage at that temperature or cone had been eliminated. In an 8 to 10-hour test, it is not possible to take out all the shrinkage at each cone, but it is possible to bring the rate of shrinkage down to a low figure.

The expansion of the furnace was calibrated with two Refrax (silicon carbide) brick whose coefficient of expansion and contraction was taken as 0.0000065 at cone 12 plus. The per cent expansion and contraction were plotted against cones. An accompanying chart gives the temperatures found for each cone.

Rate of Firing.—The rate of firing should be so regulated that each cone requires at least 30 minutes for deformation. When the shrinkage is rapid, 60 minutes per cone is better. The heat penetrates to the center of the cones, a distance of $^1/_4$ inch, more quickly than to the center of a brick, a minimum distance of which is 1.25 inches. A fast rate of heating will deform the cones but have small effect on the brick and thus will give a higher load value than a slower rate of heating.

We do not believe that it is practical to establish a single rate of heating for all kinds of fire brick. A better plan is to heat fast to 1100°C for the average fire-clay brick or 1200°C for the aluminous variety or super-refractory materials and then retard the rate of heating to about two cones per hour until the shrinking period is reached. At this point, no advance in temperature should be made until a quiescent period in the deformation of the brick is attained. Thus the time-shrinkage curves should show short pauses or a stairstep effect. This is the same treatment sought for in the ordinary cone fusion test. In order accurately to place an unknown cone in the Orton-Seger cone scale, it is necessary to "soak" the heat to the centers of the cones rather than use a surplus of heat. The curves given in the accompanying charts have been copied from the time-temperature-cone-shrinkage curves plotted during the test runs, but all have been reduced to the same cone-shrinkage basis.

High Temperature Load Value.—A numerical value was assigned to each brick as a method of estimating the relative resistance to the load at high temperatures. This value is the area in square inches under the horizontal zero shrinkage line, and under and to the left of the shrinkage curve of the brick down to 10% shrinkage. The load value increases with the cone temperature at which the brick can sustain the load, is lowered by an early shrinkage and does not include the expansion area above the zero shrinkage line. When the curves are plotted on inch cross-section paper (20 divisions to the inch) the areas can be computed easily without the aid of a planimeter. We used the ratios: one inch equals four cones (horizontal) and 4% shrinkage (vertical).

Thermal Expansion.—In each test the lever arm, by which the load was applied to the brick, raised as the furnace was heated to cone 10. With the better grades of refractories, this increase was greater than that determined for the thermal expansion of the furnace bottom and loading mechanism. Two reasons can be given for the low or zero expansion of some of the poorer grades of brick. The refractoriness may be so low that the brick deforms from fusion as fast as the furnace expands. In other cases the refractoriness may be satisfactory but the original firing in the manufacturer's kilns may have been so low that all the firing shrinkage is not out of the brick. Thus, in the case of the clay and aluminous types of fire brick, except the very siliceous ones, a medium or high thermal expansion is a good indication of refractoriness and good firing.

Type of brick	Per cent thermal expansion	Type of brick	Per cent thermal expansion
Clay	0.00 to 0.63	Chromite	1.20
Siliceous clay	0.00 to 0.86	Magnesia	2.20
Kaolin	0.75 to 1.11	Zirconia	0.52
Aluminous	0.48 to 1.53	Crystalline alumina	1.65
Recrystallized sillimanite.	1.10	Silica	2.42

It is noted in the first four types that the per cent expansion increases with the load-carrying ability of the brick from the ordinary clay to the high aluminous varieties

Testing Results

In Table I the refractories have been arranged in numerical order according to their high-temperature load-test values. A commercial recrystallized silicon carbide brick and a recrystallized sillimanite brick made in our laboratory both gave no shrinkage at cone 33, or a load value above 11.8. These were followed by a commercial crystalline alumina brick (11.2) which we refired to raise the load-test value from 9.3 and a commercial silica brick (10.62) composed of recrystallized cristobalite and tridymite. Below these lie the high aluminous brick made from diaspore or bauxite with load values ranging from 4.21 to 9.38 and the high fired kaolin brick with load values from 6.75 to 8.12. The commercial fire-clay brick have a maximum value near 5 and range from there to below 1.00. The largest number lie between 2 and 4. Commercial chromite and magnesia brick gave values of 3.8 and 4.31, respectively.

When grouped into several classes as shown in Table II, it is noted that the load-test values do not correspond with the cone of fusion or with the relative temperatures at which shrinkage starts. The load-test values correspond better with the relative temperatures at which fast shrinkage starts or the cone-temperatures at which 10% shrinkage is reached.

The two main exceptions to the load-test cone-fusion agreements are:

(1) The case of a refractory flint fire clay bonded with a poorer grade of plastic clay. Bleininger and Brown[1] in 1910 pointed out that a fire brick under load at furnace temperature is no better than its bond, which lubricates the coarse particles of refractory flint clay so that the mass

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[1] A. V. Bleininger, and G. H. Brown, "Behavior of Fire Brick under Load Conditions," *Trans. Amer. Ceram. Soc.*, **12,** 341 (1910).

softens with the partial fusion of the bond clay. In making the cones for the fusion test, standard practice[1] requires that the sample be ground to pass a No. 60 sieve. In this manner the flint clay raises the fusion point of the mixture to somewhere near the arithmetical average of the two clays. In the load test the brick slumps with the lower refractory clay.

A recent study[2] of 86 of the best Ohio fire clays showed that only 16 had cone fusion points above cone 31. Twelve of these were flint clays. Cone 33 was the highest cone fusion point. Only two bond clays gave fusion points equal to cone $30^1/_2$ and some ranged as low as cone 23.

(2) A second case is similar to the first. Chromite, magnesia, diaspore, alumina, and sillimanite brick all have very high fusion and melting points. Commercial brick made from these materials are usually mixed with plastic fire clays for bonding or as in the case of the chromite and magnesia brick they contain natural silicate impurities which act as high temperature lubricants for the refractory grains and cause early failure.

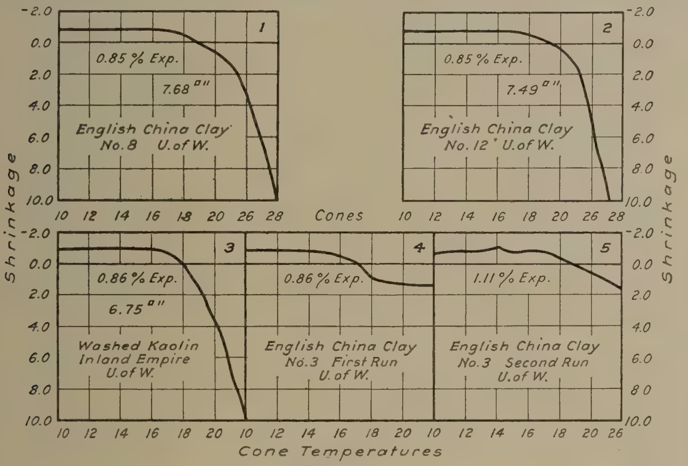

FIG. 2.

The silica, silicon carbide and recrystallized sillimanite brick were the only ones which maintained resistance to load close to their fusion or melting points. They are composed of interlocking crystals, not merely a loosely knit structure of crystalline grains, but new crystals have actually grown between the crushed grains during the firing of the brick and bind the whole mass into a strong structure. All the amorphous materials tested show early shrinkage and deformation as low as 23 cones below their fusion point.

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[1] Amer. Ceram. Soc. and the A. S. T. M.

[2] "Coal Formation Clays of Ohio," Ohio Geol. Surv., *Bull.* **26** (in press).

Individual Test Results

Nos. 1, 2, 4, 5. English china clay brick. The washed china clay from Cornwall, England, is a well-known standard material for use in porcelain and china whiteware bodies and for glazes. While approaching the theoretical kaolinite proportions of alumina and silica, analysis shows that this china clay contains a relatively large percentage of lime which is a most active high temperature flux. The cone fusion point is therefore cone 34 plus, instead of cone 35.

The raw English china clay was molded into rough brick and fired to cone 26. These were crushed and ground so that 50% passed a 2-mesh screen and was caught on a 4-mesh. Forty per cent was ground to pass a 20-mesh screen. These proportions were found by experiment to give the densest brick which could be packed by hand tamping in a steel slip mold. The fine material fills the interstices between the large grains and does not elbow them out of position. The remaining 10% was the raw, weakly plastic English china clay to which 0.2% of gum arabic had been added to increase its dry strength. After molding and drying, the bricks were fired to cone 26 at which heat they developed a white, vitreous, porcelain-like structure, though, because of defects of molding, the interior shows many blebs and holes.

The load tests indicate that the English china clay brick prepared in this manner give superior high-temperature load-resisting properties to any of the other common fire-clay brick and are inferior to only one other clay sample (No. 40), an eastern commercial kaolin brick and which we believe is made in a very similar manner. These kaolin brick surpass most of the high aluminous (bauxite, diaspore) commercial brick which have higher cone fusion points. The china clay brick were probably fired to higher temperatures and most of the commercial aluminous and clay brick contain bond clays inferior to the china clay. A pure grade of diaspore or bauxite, treated in the same manner, gives better brick than the china clay. (See Nos. 41 and 51.) In the load test, the brick will fail with the bond clay which, if inferior to the flint clay, alumina, etc., acts as a lubricant to the more refractory grains. We found that by experiment, poor molding and unbalanced grain sizes will give china clay brick which fail by shearing under load at cone 18–20.

No. 1. Sample expanded 0.85% of its original length, and maintained this to cone 17, after which it shrank gradually to cone 23 and then more rapidly at higher heat treatments reaching 10% shrinkage at cone 28. The area under the curve and the 0.0 line is 7.68 square inches which is a relative value indicating the load-resisting qualities at high temperatures.

No. 2. This English china clay brick gave a linear expansion of 0.85%, which was maintained to cone 17, but it shrank faster than did No. 1 and reached 10% shrinkage at cone 27 plus. The high temperature load value is 7.49 sq. in.

Nos. 4 and 5. These two load tests were obtained from the same brick. In the first the temperature was only raised to cone 23 and because of the failure of the alundum plunger which applied the load, the test was discontinued. After the second test to a maximum of cone 26, the brick had only shrunk a total of 4.85% for both tests. This is but 0.85% above the allowable maximum in the American Society for Testing Materials' load test for heavy duty fire brick at 1350°C (cone 14 approximately).

No. 3. The kaolins of eastern Washington and northwestern Idaho are similar to the English china clay. The original material in both fields requires the removal of quartz, mica, and some feldspar. The Inland Empire kaolins provide a supply of raw material for a future whiteware pottery industry.[1]

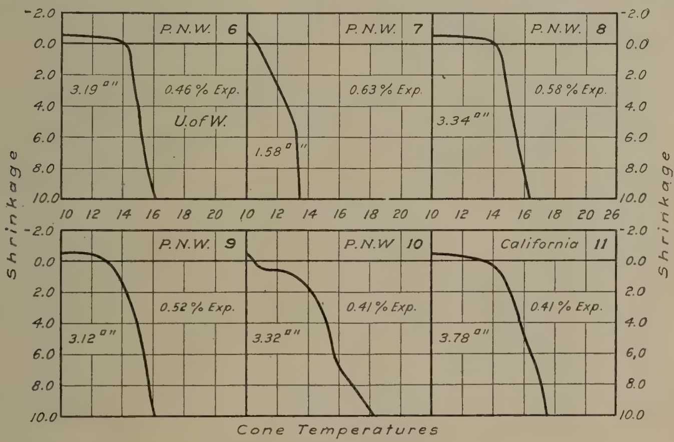

FIG. 3.

At the present time, the run-of-mine kaolin material is used in the manufacture of siliceous fire-clay brick at four factories. Test No. 3 (University of Washington brick) gave a load test but slightly inferior to the best of the English china clay brick and superior to most of the other fire-clay and high aluminous commercial brick. The Inland Empire kaolins, therefore, offer the opportunity for the production of the highest quality fire-clay brick.

It is not expected that the quantity of such brick will be great for the manufacturing costs will be high, but a few should be made to meet the special demands for a superior article. A few such brick in the hottest parts of the furnaces with the ordinary brick for the remainder will give a more uniform life to the furnace wall, will prevent shutdowns to renew but a small portion of the wall, will make it unnecessary to send east for the high aluminous (diaspore) brick, mortars and patching compounds, and will give the manufacturer a better chance to sell his ordinary product for the rest of the job.

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[1] H. Wilson, A. L. Bennett, and F. T. Heath, "Preliminary Report on the Residual Kaolin and Feldspar in the Pacific Northwest," *Jour. Amer. Ceram. Soc.*, **6** [3], 475 (1923).

No. 6. A brick made at the University of Washington of the ground fire clay from a Pacific Northwest company. It was fired about three cones higher than the usual commercial product, and, as a result, the high-temperature load value was doubled. After the load test the brick shows a blackened interior which has developed a vitreous and brittle structure. Maximum expansion, 0.46%. High-temperature load value, 3.19.

No. 7. A commercial Pacific Northwest brick which fails under load before cone 14 and develops a blackened vesicular structure at cone 16. Maximum expansion, 0.63%. High-temperature load value, 1.58.

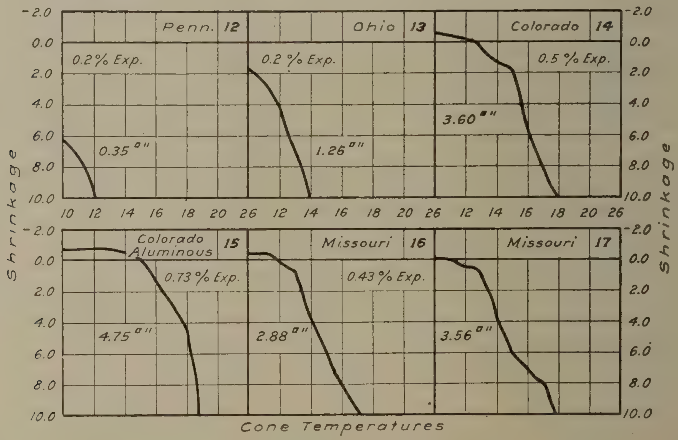

FIG. 4.

Nos. 8, 9, 10 are commercial siliceous Pacific Northwest brick which gave similar load tests. The break in the curve of No. 10 at cone 10–11 is probably due to a low firing in the manufacturer's kilns. After this shrinkage is eliminated, the brick maintains considerable rigidity. Early shrinkage does not always indicate early failure. The quartz content of the siliceous brick keeps the body open and porous after heat treatment to cone 18.

No. 11 is a commercial California siliceous brick in which the quartz particles are surrounded by a high-grade fire clay instead of a kaolin-mica mixture.

No. 12 is a commercial brick made of a Pennsylvania flint fire clay bonded with an inferior bond clay which fuses and develops a vesicular structure at a very low cone. The brick had already shrunk over 6% at cone 10. The maximum expansion is also low as the shrinkage started before the usual expansion of the furnace was complete.

No. 13 is likewise an example of the poor load carrying behavior of an Ohio flint clay bonded with an inferior bond clay.

No. 14 appears to be a mixture of two or more clays, some of which are refractory and white-burning, and others are fused, blackened and vesicular at cone 18. Black slag spots oozed out on the surface of the brick. The brick tested were from Colorado.

No. 15 is one of the commercial aluminous brick from Colorado which has maintained an open porous structure and shows no signs of fusion or sintering to the eye on the fractured surfaces and yet has shrunk 10% in length and, in some cases, shows curved edges and deformation of shape due to shrinkage when partially soft. The very high fusion point (cone 37) indicates that the refractoriness has not been severely tried at cone 19. The load-test values of this type of material will vary with the original temperature of firing in the manufacturer's kilns, unless a low-fusing bond clay is used. However, brick in which an interlocking crystalline framework has developed, are the only ones which we have found yet, which will resist loads up to their cone fusion or melting temperatures.

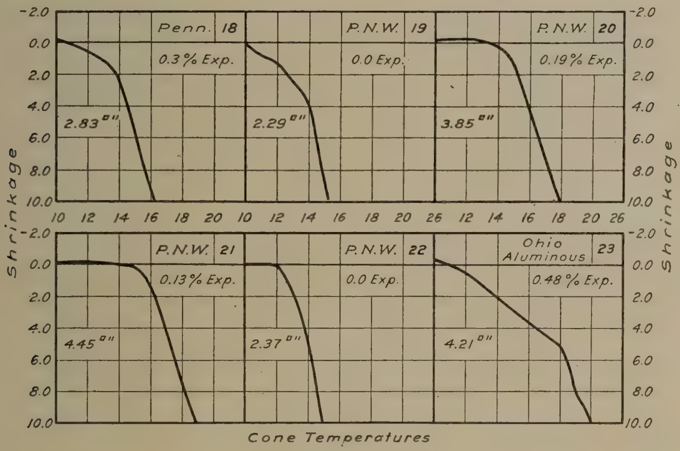

FIG. 5.

Nos. 16 and 17 are examples of the better grades of fire clay which fire to a dense structure at cone 18–19. No. 16 is composed almost entirely of one type of clay and contains iron compounds which fuse to black slag spots on reheating. No. 17 apparently is formed of two kinds of fire clay, one of the plastic bond type and the other of the flint type.

No. 18 is a well-known commercial brand consisting of coarse particles of Pennsylvania flint fire clay bonded with a less refractory plastic fire clay. The latter is the deforming member of the mixture and prevents the brick from reaching a higher class in the load test.

No. 19 is a commercial product made from one of the light-colored siliceous clays and contains a few dark-colored iron spots. Shrinkage started before the furnace parts had reached their maximum expansion and no apparent expansion of the brick was therefore noted. This early shrinkage is undoubtedly caused by underfiring. The early final shrinkage is due in part to the rupture of the brick along planes caused by auger and die lamination. The brick has not been repressed.

Nos. 20 and 21 are examples of the siliceous light-colored brick which contain but little flux. The expansion of the quartz tends to counteract the shrinkage of the kaolin-like clay bond. After the refiring in the load test, the brick have a punky structure, quite different from the non-siliceous vitrifying type of fire clay.

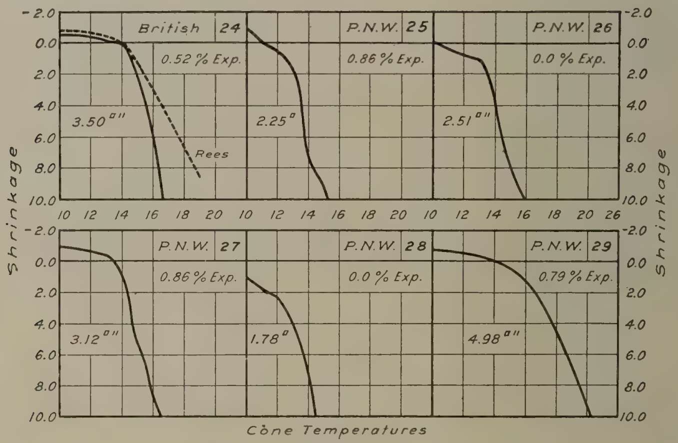

FIG. 6.

No. 22 is composed of a single fire clay which does not give a very good load test value due both to a low initial temperature of firing and to early vitrification and fusion. In this load test the brick was carried to cone 23 although it reached 10% shrinkage at cone 15. At cone 23 the sample was bloated and vesicular.

No. 23 is a commercial brick consisting of Missouri diaspore bonded with an Ohio bond clay. The initial firing temperature has not been sufficient to prevent an early shrinkage but when this has been eliminated the brick did not reach 10% shrinkage until nearly cone 20. Its refired structure is much denser and more nearly vitrified than the other aluminous brick.

No. 24 is a sample of a British fire clay brick. It is not a mixture of flint and plastic fire clay but two or more similar fire clays may have been used in the batch. It reached 10% shrinkage before cone 17. The load was removed at cone 20 and, as its companion in the load test was a silica brick, it was carried to cone 31. At this temperature the British brick had softened to an irregular fused mass five inches high. The dotted curve shows a similar load test reported by W. J. Rees of the Sheffield University, England. The thermal expansion obtained by Dr. Rees is 0.8%.

Nos. 25, 26, 27, 28, and 29 are all commercial Pacific Northwest siliceous brick varying in firing treatments, quartz contents and impurities. No. 29, with a load test value of 4.98 is remarkable because of the comparatively low cone fusion (31 plus). This load test value is in the present aluminous refractory class. We believe that this result is obtained by a combination of a high-kaolin content plus a high temperature of firing. A few quartz grains are noted in the broken cross-section.

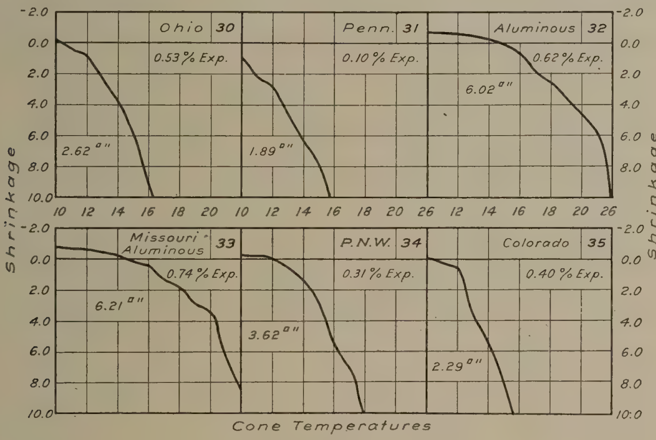

FIG. 7.

Nos. 30 and 31 are commercial brick made from eastern flint fire clays and plastic bond clay mixtures. The flint fire clays are very refractory but the bond clays are inferior. The latter deform under load and lubricate the coarse particles of flint fire clay so that the whole mass slumps easily. However, the cone fusion temperatures lie between cones 32 and 33. When ground to pass a 60-mesh sieve the average cone fusion of the two clays is found. A. V. Bleininger in 1912,[1] suggested the use of the minimum amount of plastic bond clay and also the grinding of the plastic bond clay with some flint clay to improve the refractoriness of the former.

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[1] "The Testing of Clay Refractories, with Special Reference to their Load Carrying Capacity of Fur. Temps.," U. S. Bur. Stand., *Tech. Paper* **7**, p. 11.

The development of the plasticity of a flint fire clay was increased by wet-pan grinding.[1]

Nos. 32 and 33 are two examples of the aluminous brick made from Missouri diaspore and fire clay. While made by two different companies the load test values are very similar. See Nos. 15 and 23.

No. 34 is another Pacific Northwest kaolin-like brick similar to No. 29.

No. 35 is a mixture of several clays from Colorado, some of which produce fusible iron slag spots. One fires to a dense vitreous gray body, like a flint fire clay and another to a more open buff structure.

Nos. 36 to 39 are four commercial fire-clay brick, two from the Pacific Northwest and two from Sweden.

No. 40 is an eastern commercial kaolin brick probably made in a manner similar to that described for the English china clay brick (Nos. 1, 2, 4, 5).

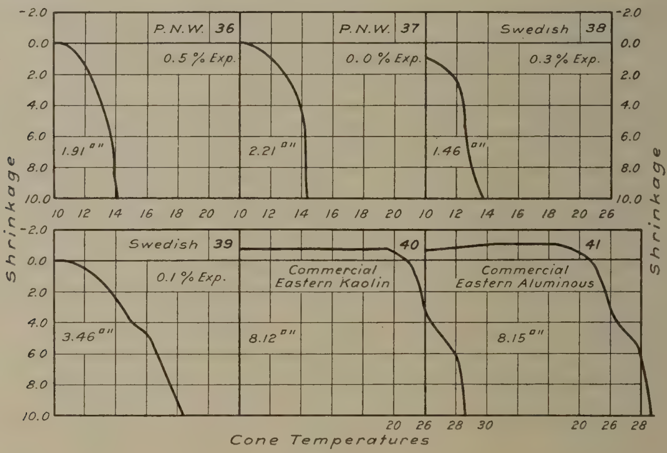

FIG. 8.

It gave the best load test of any clay brick and exceeded all but two of the aluminous variety. Its high temperature rigidity is due to a combination of refractory bonding and an initial high-temperature firing.

Nos. 41 and 51. Show the load tests of commercial high-aluminous brick which have been well bonded and fired to high temperatures.

No. 42. Chromite brick. While the maximum expansion for any fire-clay brick was 0.86%, the chromite brick had an expansion of 1.3%. Curve No. 1 shows the load test behavior of the chromite brick as received from the manufacturer. Curve No. 2 shows the test repeated for another chromite brick which was reheated to above cone 30 for over 12 hours. This high temperature soaking treatment increased the load carrying value of sillimanite brick by producing an intergrowth of crystals between the crushed sillimanite grains. Some such result has started with the chromite brick but it contains too much silicate impurity to resist crushing under light loads beyond cone 18–19. The more easily fusible silicates soften and lubricate any crystalline or amorphous refractory grains and easy separation follows. The brick of test No. 1 is friable and the grains are loose. The brick of test No. 2 is much harder and while it sheared in several planes, the broken pieces adhered together very strongly, showing that some portion had fused but had hardened again on cooling. Chromite brick shear along a diagonal plane suddenly and behave quite differently from the amorphous clay brick whose length diminishes while the cross-section increases. The cone fusion point of the chromite brick is above cone 42.

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[1] See E. F. Goodner, "Four Typical Refractory Clays of Washington," Thesis, University of Washington.

No. 43. Magnesia brick. Curve No. 43 shows the high temperature load test of a commercial brick made in the east from Washington magnesite. The brick expands to 2.2% which is reached at cone 13 and maintained to cone 15. After only 4.2% contraction, the brick shears suddenly at cone 17 in a similar manner to the chromite brick. While no softening of the larger magnesia grains has occurred, the iron-alumina-lime-silicate impurities have fused and lubricated the interior structure of the brick. One of these magnesia brick was reheated with the chrome brick to above cone 30 to improve the load carrying ability at high temperatures. The magnesia brick standing on end gave way under its own weight during the soaking period, and parts which came in contact with the high aluminous clay lining of the furnace fluxed the latter very badly. The edges of the brick were curved and vertical cracks opened up showing clearly that the brick had softened.

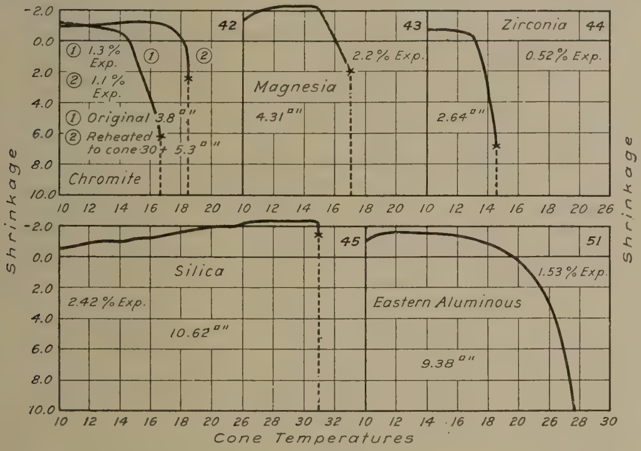

FIG. 9.

No. 44. Zirconia brick. While pure zirconia has a melting point in the neighborhood of 2900°C, this commercial brick apparently contains too much silicate impurities or added bonding clay to give a high-temperature load test above a lower grade of fire-clay brick. The brick sheared after a contraction of 7% between cones 14 and 15. The cone fusion point indicates a very refractory material. A reheating test was tried on another zirconia brick. However, it was necessary to remove the zirconia brick from the furnace when cone 30 was first reached owing to the bloating and fusion. Gases formed within a vitrified surface have bloated the brick and have produced a very pronounced vesicular structure.

No. 45. Silica brick. Figure 45 shows the load test curve of a well-known eastern brand of silica brick. A previous test on two other brick to cone 28 followed this curve and gave no shrinkage. Because of the rapid volume changes, the cooled brick were punky but they were able to carry the 25 pound per square inch load to very high temperatures. The curve given shows a sudden failure by shearing at cone 31 after a maxi-

TABLE I

Number	Load test value	Cone fusion	Per cent maximum expansion	Start of shrinkage cone	Start of fast shg. cone	10% shrinkage cone
50	Above 11.8	Dissociates	0.84	Above 33	..	..
49	Above 11.8	39	1.1	Above 33	..	..
47 (2)	11.2	39–40	2.0	29 (+)	30	32 (+) (shear)
45	10.62	32–33	2.42	30–31	30–31	31 (+) (shear)
51	9.38	40	1.53	15	20	28
47 (1)	9.31	39–40	1.3	23	23	31 (shear)
41	8.15	38 (+)	1.12	19	20–23	28–29
40	8.12	33½	0.75	19–20	23	28–29
1	7.68	34 (+)	0.85	17	23	28
2	7.49	34 (+)	0.85	17	23	27 (+)
3	6.75	34	0.86	16 (+)	18	26
33	6.21	37	0.74	12	20	26
32	6.02	35	0.62	12–13	18	26 (−)
42 (2)	5.3	42	1.1	16	18 (+)	18–19 (shear)
29	4.98	32	0.79	10	16	20 (+)
23	4.96	35	0.32	12–13	14	20–23
15	4.75	37	0.73	13	15	19
21	4.45	30	0.13	13	15	19
43	4.31	..	2.2	15	15	17 (shear)
27	4.23	30–31	0.86	10	13–14	26
20	3.85	30	0.19	12	15	18 (−)
42 (1)	3.80	42	1.3	10	14–15	16–17 (shear)
11	3.78	28–29	0.41	10	14	17–18
34	3.62	31 (+)	0.31	11	13	18
14	3.60	30–31	0.5	10	15	18
17	3.56	32	..	10	13	18 (−)
24	3.50	31 (−)	0.52	10	14	16–17
39	3.46	33 (−)	0.10	11	12	18 (+)

8	3.34	31	0.58	12	14	16–17
10	3.32	31	0.41	10	13	18 (+)
6	3.19	30 (+)	0.46	11	14	16
9	3.12	31	0.52	11	13	16
16	2.88	31	0.43	11	13	17 (+)
46	2.87	Above 42	0.06	14	14	14–15
18	2.83	32	0.3	10	14	16 (+)
44	2.64	37	0.52	11	13	14–15
26	2.62	29 (+)	0.0	10	13	23
30	2.62	32 (+)	0.53	Before 10	12	16 (+)
22	2.37	28 (−)	0.0	12	12	15
19	2.29	30	0.0	10	12	15 (+)
35	2.29	30–31	0.40	Before 10	12	15–16
25	2.25	30 (+)	0.86	10	12	15 (+)
37	2.21	30	0.0	10	12	14 (+)
36	1.91	28–29	0.5	10	11	14
31	1.89	33 (−)	0.10	Before 10	10	15–16
28	1.78	28	0.00	Before 10	12	14–15
7	1.58	27 (+)	0.63	10	10	13–14
38	1.46	28	0.30	Before 10	12	14 (−)
13	1.26	30 (−)	0.20	Before 10	10	14
12	0.35	28 (−)	0.20	Before 10	Before 10	12 (+)

mum expansion of 2.42% which was not reached until above cone 26. All of the other brick preceding the silica brick have deformed under load far below their cone fusion points. The silica brick has the ability to maintain a rigid load carrying structure to within 1–2 cones of its softening point under no load. This property is characteristic of pure crystalline materials which do not gradually soften but melt suddenly at a definite temperature. Commercial silica brick contain only 5 to 6% of cal-

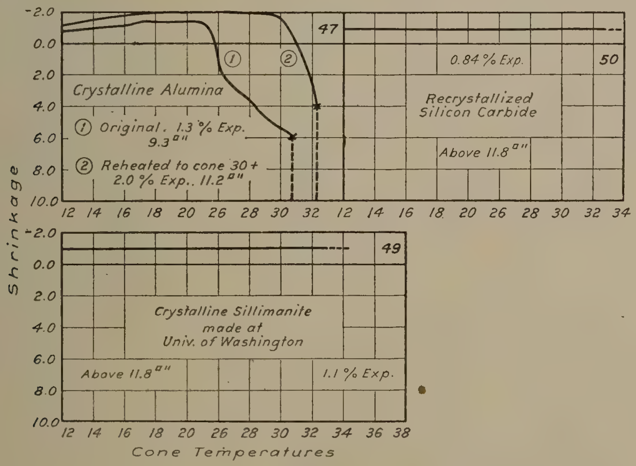

FIG. 10.

cium-alumina-silicate impurities and the original quartz crystalline fragments have been partially recrystallized and bonded with the intergrowth of tridymite and cristobalite crystals. While the final melting point is comparatively low, silica brick are the only brick which have been used successfully in carrying the loads of long flat arches for high-temperature furnaces such as the open-hearth steel furnace. This would indicate that if higher temperatures beyond the melting point of the silica brick are needed, it will be necessary to produce another recrystallized refractory from the group of super-refractories.

No. 47. Crystalline alumina. Curve No. 1 shows the load heat test of a commercial crystalline alumina (corundum) brick, as received from the manufacturer. After a maximum expansion of 1.3% from cones 17 to above cone 20, the brick shrunk rapidly to cone 26 and then at a slower rate to nearly cone 31 where it failed by shearing. In the neighborhood of cone 26 the formation of sillimanite is rapid and this would retard the shrinkage. The silicates of the bonding clay would unite with the finely ground corundum to form sillimanite. On reheating another sample of this brand to above cone 30 a better load-test curve was obtained. The greater expansion (2.0%) which persists to cone 29, shows that a partial crystalline intergrowth has been produced. Apparently the quantity of impurities is sufficient to cause a failure by shearing before that of a relatively pure sillimanite brick.

TABLE II

Class	Load value	Cone of fusion	Start of shrinkage cone	Start of fast shg. cone	10% shrinkage cone
1	Undeformed	( )–39	Above 33	.....	.....
2	Above 10	32–40	29–31	30–31	31–32
3	5–10	32–42	10–18	14–23	18–31 (–)
4	4–5	30–37	10–15	13–15	17–26
5	3–4	28–42	10–12	12–15	16–18
6	2–3	29–32 (+)	Before 10–14	12–14	14–23
7	–2	27–33 (–)	–10	Before 10–12	12–(15–16)

No. 49. Crystalline sillimanite made at the University of Washington. This material was made by melting English china clay and pure alumina in the electric furnace. The recrystallized sillimanite brick were able to carry the load to above cone 33 without any shrinkage or signs of deformation. The plastic bonding material consisted of 10% of a mixture of raw china clay and alumina in the proportions to produce sillimanite, with 0.2% gum arabic.

No. 50. Crystalline silicon carbide. This is the load test of a commercial brick composed entirely of SiC. The silicon carbide is made by heating silica and carbon in an electric resistance furnace. The brick are molded by aid of an organic bond and fired in a second electric resistance furnace to very high temperatures so that the crushed crystalline fragments are locked together with a growth of new crystals. We are not able to cause failure of this brick after heating to cone 33, although under oxidizing conditions small samples of silicon carbide are dissociating very rapidly accompanied by bubbling at 1650°C.

No. 51. See No. 41.

NOTE: We wish to acknowledge the help received from members of the U. S. Bureau of Mines Experiment Station staff in preparing the sillimanite brick, and to F. W. Schroeder and H. C. Fisher, "fellows," University of Washington, for assistance with the load tests.

DEPARTMENT OF CERAMIC ENGINEERING
UNIVERSITY OF WASHINGTON

THE MANUFACTURE OF AN INSULATING BRICK FROM DIATOMACEOUS EARTH

By C. A. Smith

ABSTRACT

Development of an Insulating Brick.—Pulverized diatomaceous earth was blended with each of the four clays, Tennessee ball, Bedford shale, Rock Hill, Tionesta, in percentages of 0, 5, 10, 15, 20, 30, 50 clay. Dry pressed briquettes were made using 50 to 60% water, and were burned at cones 06, 02 and 2. Heat conductivity tests were made upon the best bodies of the series.

Introduction

The purpose of this thesis is the development of a method of producing an insulating brick from crushed or powdered diatomaceous earth.

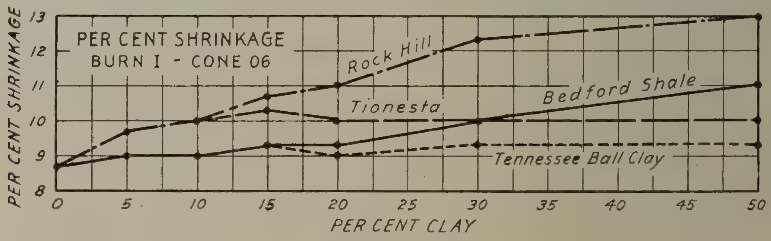

Fig. 1.

A great amount of crushed material is produced in mining this material and at present there is an excess of this crushed material over that needed in the industries.

Diatomaceous earth is also called infusorial earth, bergmehl, tripoli, moler, fossil earth, white peat, celite, kieselguhr, and sometimes erroneously referred to as "desmid earth," and is widely distributed in deposits in the United States and Europe in varying degrees of purity. Strictly speaking, it is composed of the microscopic skeletons of bacillariae or diatoms,

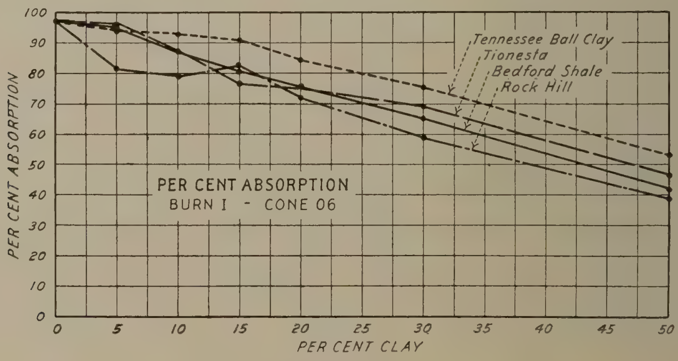

Fig. 2.

one of the groups of flowerless salt and fresh-water plants of the species "algae."

The chief impurities are diatomaceous silt, clay, sand or volcanic ash, and other inorganic materials. The chief deposit in the United States is near Lompoc, Santa Barbara County, Calif. This is of exceptional purity. The material occurs in beds of minimum thickness of seven hundred feet, ranging from soft material to hard black flint, and as mined, contains from 25 to 40% H_2O, which can be expelled at 100°C.

COMPOSITION OF MATERIAL IN LOMPOC DEPOSIT[1]

	1	2	3		1	2	3
SiO_2	88.78	85.28	94.59	MgO	1.3	1.30	trace
Al_2O_3	2.68	5.35	1.87	Ignition loss	5.54	5.57	2.22
FeO	trace	1.12	0.76	Color	white	ivory	white
TiO_2	0.10	0.21	0.10	Color after ignition	white	pink	white
CaO	1.61	1.12	0.83				

1. Very light, pure white diatomaceous earth.
2. Light weight, brownish diatomaceous earth.
3. Compact diatomaceous shale.

The true specific gravity of this earth is from 2.1 to 2.2 at 25°C, and in block form, as quarried, the apparent specific gravity is about 0.45 or approximately twenty-eight pounds per cubic foot. When loosely packed, the apparent specific gravity is approximately 0.13, or eight pounds per cubic foot.

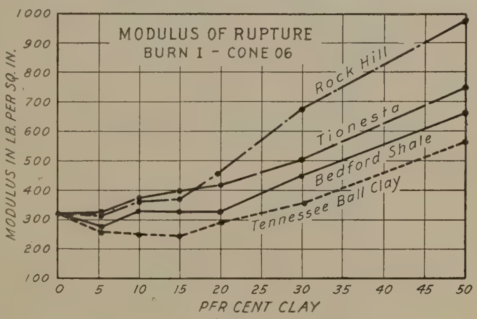

FIG. 3.

Outline of Procedure

The following method of procedure was adopted:

1. Mixtures of diatomaceous earth and clay in proportions of 5, 10, 15, 20, 30 and 50% of clay by weight were made up with four types of plastic clay. The clays were ground to pass an 80-mesh sieve.

The diatomaceous earth was the standard commercially air-separated material, sold in bags, and used as heat insulating material.

2. The dry materials were thoroughly mixed by hand, moistened with water and again mixed thoroughly by hand. Sixty per cent of water was added to the 0–5–10–15% clay mixtures, and 50% to the 20–30–50% clay mixtures. This amount of water made the material suitable for dry pressing.

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[1] *Met. and Chem. Eng.*, **12,** 109 (1914).

3. Briquettes, 1 x 1 x 4 inches, were made in a press. Shrinkage marks were impressed and the briquettes then dried for forty-eight hours at approximately 75°C (170°F). The drying shrinkage in all cases was negligible.

4. Four trials of each body were fired at cones 06, 02 and 2. The cone 06 and cone 02 burns were made in a gas-fired muffle kiln, the briquettes being hacked very openly five high. The cone 2 burn was made in a direct gas-fired kiln in open saggers, being widely spaced in the saggers.

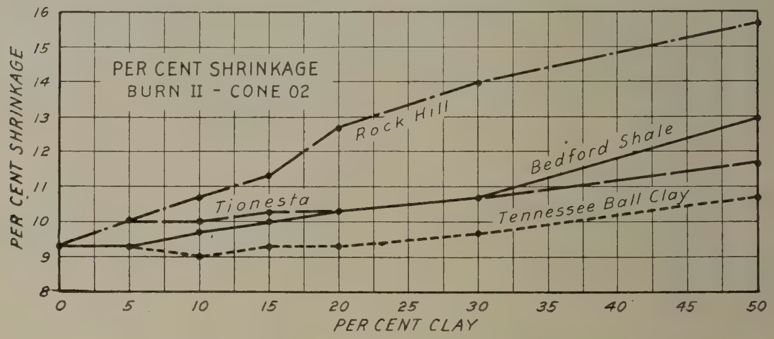

FIG. 4.

5. The trials were tested for shrinkage, absorption, and modulus of rupture. In breaking the briquettes, a Riehlé load testing machine was used for bars breaking at seventy-five pounds and over, while bars breaking at lower loads were broken by pouring lead shot into a bucket at a constant rate.

Due to limit in time, heat transfer tests were made only on those tile having high absorption, low shrinkage and fair modulus of rupture. The

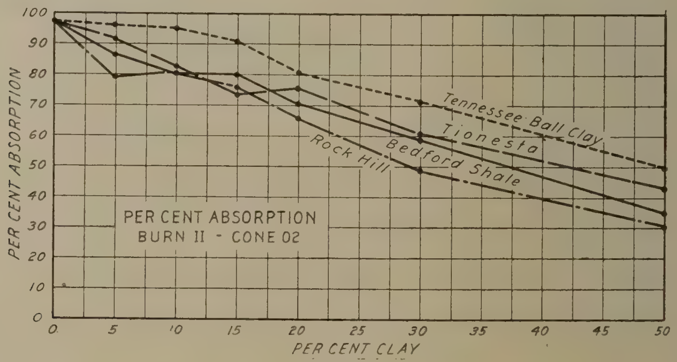

FIG. 5.

figures given represent the ratio of the heat transferring ability of the sample tested to that of a standard material having an index of 1.0. This standard is Alundum. According to this classification, ordinary sawed diatomaceous earth block has an index of 0.263. "Carbofrax B" (92% Si C) has an index of 3.39, and magnesite an index of 2.33. Thus the smaller the index, the greater the insulating ability of the material, and vice versa.[1]

TABLE I

RESULTS OF BURN I—CONE 06

Fired to cone 06 down in 24 hours, cooled 12 hours and ware removed.

Briquette Serial No.	Average per cent total shrinkage	Average per cent absorption	Average modulus, lbs. per sq. in.
100% Diatomaceous earth	8.7	97.2	320.0
[1]B-5	9.0	94.8	263.0
B-10	9.0	86.8	330.5
B-15	9.3	81.0	326.0
B-20	9.3	75.4	326.5
B-30	10.0	64.7	448.5
B-50	11.0	41.7	659.5
[2]T-5	9.7	96.4	324.0
T-10	10.0	87.1	371.5
T-15	10.3	76.4	397.5
T-20	10.0	74.8	417.0
T-30	10.0	68.8	502.0
T-50	10.0	46.1	745.5
[3]TB-5	9.0	94.4	259.0
TB-10	9.0	92.8	249.0
TB-15	9.3	90.7	243.0
TB-20	9.0	84.4	288.0
TB-30	9.3	75.2	353.0
TB-50	9.3	53.0	559.0
[4]R.H.-5	9.7	81.4	313.0
R.H.-10	10.0	79.0	362.5
R.H.-15	10.7	82.3	370.0
R.H.-20	11.0	71.8	456.0
R.H.-30	12.3	58.4	674.5
R.H.-50	13.0	38.4	979.0

[1] B—Bedford shale.
[2] T—Tionesta.
[3] TB—Tennessee ball.
[4] R.H.—Rock Hill.

Observations in Molding Briquettes

The soft or stiff mud process of making brick could not be used successfully with a diatomaceous earth low in clay. First of all, the material has not enough plasticity to enable it to hold together in being forced through a die, and, second, the material will absorb such large quantities of water before it becomes wet, that it would be impractical to mix it to the necessary consistency in a pug mill, due to the very strong tendency to form balls of damp material having an outer coating of dry diatomaceous earth. While diatomaceous earth can be molded by dry pressing without any clay bond and with 60% water, the briquette is very weak and will stand very little handling. Clays in percentages of 5–10–15 do not affect the strength greatly but percentages of 20–30–50 have a very decided effect on the molding properties. The 20 to 50% clay briquettes could be handled by careful workmen.

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[1] A. S. Watts and R. M. King, "The Method of Measuring Heat Transfer Values," *Jour. Amer. Ceram. Soc.*, **6** [10], 1075 (1923).

Since it was found that clay, in amount of 20% and over, was satis-

TABLE II

RESULTS OF BURN II—CONE 02

Fired to cone 02 down in 28 hours, cooled 12 hours and ware removed.

Briquette serial no.	Average per cent total shrinkage	Average per cent absorption	Average modulus, lbs. per sq. in.
100% Diatomaceous earth	9.3	97.0	377.0
B-5	9.3	86.4	379.0
B-10	9.7	80.2	415.5
B-15	10.0	80.2	420.0
B-20	10.3	70.5	379.7
B-30	10.7	58.7	580.5
B-50	13.0	34.6	1077.0
T-5	10.0	91.3	430.5
T-10	10.0	82.6	563.0
T-15	10.3	73.7	543.0
T-20	10.3	75.7	518.3
T-30	10.7	60.8	748.0
T-50	11.7	43.1	1082.0
TB-5	9.3	96.5	208.0
TB-10	9.0	94.7	258.5
TB-15	9.3	90.6	294.0
TB-20	9.3	80.5	350.5
TB-30	9.7	71.3	442.0
TB-50	10.7	49.4	609.3
R.H.-5	10.0	79.1	404.0
R.H.-10	10.7	80.6	400.0
R.H.-15	11.3	75.3	494.5
R.H.-20	12.7	66.1	704.5
R.H.-30	14.0	48.6	980.0
R.H.-50	15.7	30.2	1270.0

		Per cent shrinkage	Per cent absorption	Modulus, lbs. per sq. in.	Heat transfer value
First choice	20% Tenn. ball.	9.3	80.5	350.5	0.321
Second choice	20% Tionesta...	10.3	75.7	518.3	0.292
	100% Diat. earth..	9.3	97.0	377.0	0.274

factory in the raw state, no amount less than that will be considered in the choice of a mixture.

		Per cent shrinkage	Per cent absorption	Modulus, lbs. per sq. in.	Heat transfer value
First choice	20% Tenn. ball........	9.0	84.4	288	0.252
Second choice	25% Tenn. ball........	9.2	80.0	320	0.280
Third choice	20% Bedford shale.....	9.3	75.4	326.5	...
	100% Diat. earth........	8.7	97.2	320	0.274

The Rock Hill clay shows a very marked degree of vitrification, producing a dense brick unsuited for good insulating.

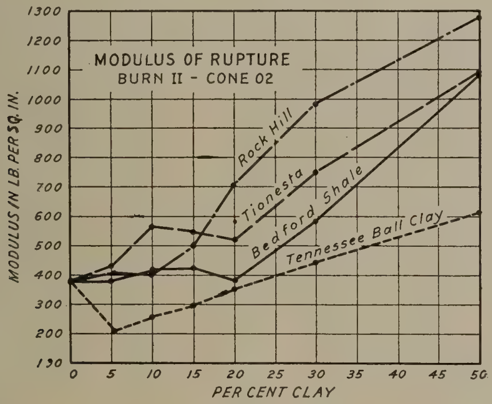

FIG. 6

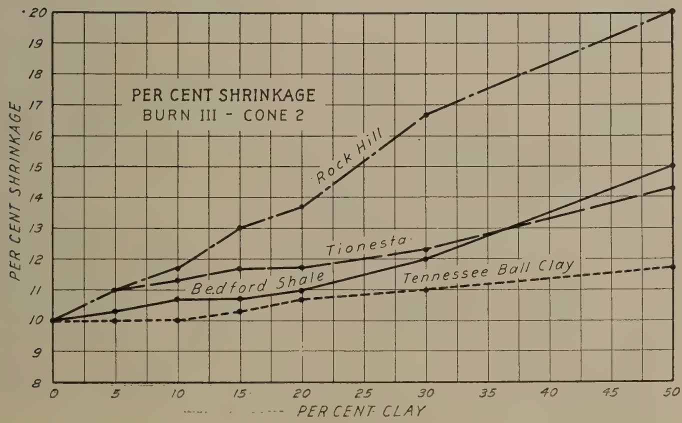

FIG. 7.

Bedford shale and Tionesta are starting to tighten up in clay percentages of 20 to 50%, and Tennessee ball clay mixtures of 30 to 50% are becoming too dense for a high grade insulating material.

All the clay bodies increased in density to such an extent that the insu-

TABLE III

RESULTS OF BURN III—CONE 2

Fired to cone 2 down in 24 hours, cooled 18 hours and ware removed.

Briquette serial no.	Average per cent total shrinkage	Average per cent absorption	Average modulus, lbs. per sq. in.
100% Diatomaceous earth	10.0	92.0	535.0
B-5	10.3	88.8	479.5
B-10	10.7	78.5	582.0
B-15	10.7	76.7	625.0
B-20	11.0	68.1	552.7
B-30	12.0	54.8	827.0
B-50	15.0	28.7	1552.0
T-5	11.0	81.5	717.0
T-10	11.3	80.2	725.0
T-15	11.7	72.3	815.0
T-20	11.7	69.0	773.0
T-30	12.3	55.9	1068.0
T-50	14.3	36.8	1571.0
TB-5	10.0	86.1	402.0
TB-10	10.0	89.0	380.0
TB-15	10.3	81.6	494.0
TB-20	10.7	74.6	607.5
TB-30	11.0	64.9	589.5
TB-50	11.7	43.6	722.0
R.H -5	11.0	73.9	630.0
R.H.-10	11.7	82.7	562.5
R.H.-15	13.0	73.1	763.0
R.H.-20	13.7	59.9	1013.5
R.H.-30	16.7	41.4	1504.0
R.H.-50	20.0	17.8	2827.0

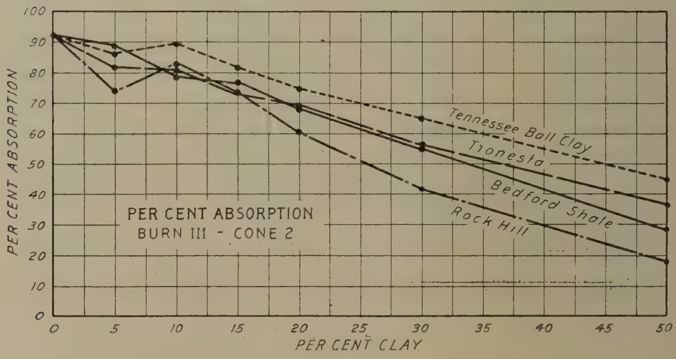

FIG. 8.

lation value was much inferior to pure diatomaceous earth and to that of the ware of the previous burns, but it was still sufficient for them to be classed as good insulators. The best bodies were as follows:

		Per cent shrinkage	Per cent absorption	Modulus, lbs. per sq. in.	Heat transfer value
First choice	20% Tenn. ball . . .	10.7	74.6	607.5	0.364
Second choice	20% Bedford shale	11.0	68.1	552.7	. . .
	100% Diat. earth. . .	10.0	92.0	535.0	0.351

Summary of Results of All Burns

A body composed of 80% of diatomaceous earth and 20% of Tennessee ball clay is satisfactory for dry pressing into brick, using 50% water. The clay and the diatomaceous earth should be mixed thoroughly dry before any water is added, and after adding water, the materials must be again thoroughly mixed. In factory practice, the dry mixing could be done in tube mills containing *Z* bar projections, and the water could be added as is done in dry press porcelain insulator manufacture, after which the body should be put through a high speed disintegrator to more uniformly distribute the moisture and to pulverize the material.

This body, when burned at cone 06, produces high absorption, low increase in shrinkage, and a modulus of rupture sufficiently high for the purpose of insulation.

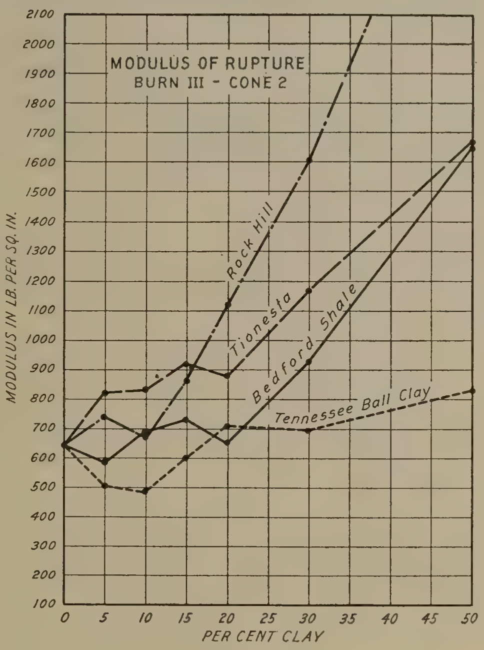

FIG. 9.

The properties of the first and second choice bodies are:

		Per cent shrinkage	Per cent absorption	Modulus, lbs. per sq. in.	Heat transfer value
First choice	Tenn. ball 20%. . . . Cone 06	9.0	84.4	288	0.252
Second choice	Tenn. ball 20%. . . . Cone 02	9.3	80.5	350.5	0.321
	Tenn. ball 25%. . . . Cone 06	9.2	80.0	320	0.280

The resistance to abrasion of the two second choice bodies is of equal quality, and is slightly greater than first choice, so if this property is more desirable than absorption (as in very long shipping), greater resistance to abrasion may be obtained by either an increased fuel cost or an increased cost of material, *i. e.*, clay.

The above results prove conclusively that a commercially satisfactory insulating brick can be made from pulverized diatomaceous earth and clay by the dry press process, if care is taken in pulverizing the materials, in thoroughly mixing of materials, both when dry and wet, and in handling of ware in the unburned state. These brick, while not equal in insulating value to the quarry sawed diatomaceous earth block, are so much superior in other physical properties that they should be able to supply an extensive market.

Acknowledgment

NOTE: The author wishes to hereby express his appreciation and acknowledgment of the many helpful suggestions of A. S. Watts, under whom this thesis was conducted.

THE DEAD BURNING OF DOLOMITE.—I[1]

By James Thomas Robson and James R. Withrow[2]

This is the first of a series of articles covering the second phase of an investigation by the U. S. Bureau of Mines, in coöperation with the Ohio State University, into the possibility of utilizing dolomite as a base material in the manufacture of refractories.

Introduction

Dolomite, a double carbonate of lime and magnesia having the theoretical formula $CaCO_3MgCO_3$, when formed and burned into bricks possesses the undesirable property of disintegrating when standing in the air, due to the slaking of the lime content. Since dolomite is very abundant and possesses great refractoriness together with basic properties similar to magnesite, it is very desirable that this serious slaking defect be overcome so that it may act as a substitute for the more expensive magnesite.

This work was carried on (1) to obtain dolomite in the dead burned form, and (2) to investigate the feasibility of producing standard size bricks of dead-burned dolomite composition.

The term "dead burned" dolomite signifies dolomite which is in the stable form after burning and will not slake down upon prolonged exposure to the atmosphere.

The total apparent consumption of crude magnesite in the United States for 1921, amounted to 113,479 short tons of which 58% was imported.

Normal consumption of magnesite in the United States, in terms of crude, amounts to about 300,000 tons of which a large part is dead burned and consumed by the steel and other metal industries. The year 1921, therefore, resulted in an apparent consumption of but little more than a third of this amount. This was due to the slump in the metal industries.

The entire domestic production of 47,904 tons came from California. That state produces but little dead-burned material, most of the ore being sold as caustic magnesite for other than metallurgical work.

The estimated value per ton of domestic crude ore was $10.65 as against $10.01 for the imported material. The total value of imported magnesite was $525,452 and that of the domestic production $510,177. Of total imports but 6,788 tons were calcined, the remainder 51,993 tons having been brought in as crude. This was probably due to fuel and labor conditions at the point of shipment.[3]

On February 6, 1923, crude magnesite was quoted at $14.00 per ton and calcined magnesite $40.00 per ton f. o. b. California points. The dead-burned magnesite grains were quoted at $40.00 per net ton f. o. b. at Baltimore and at $40.50 and $42.00 at Chester, Pa. Magnesite bricks, nine-inch straights were quoted at $65.00 and $68.00 per ton f. o. b. the works. At the same time, dolomite one-half inch and larger was quoted at $1.10 and $1.35 per net ton at New York state shipping points.

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[1] Published by permission of the Director, U. S. Bureau of Mines.

The first phase of the work has been in three previous arcticles by H. G. Schurecht as cited.

The authors are indebted to G. A. Bole, A. S. Watts and W. J. McCaughey for valuable suggestions.

Magnesite refractories are used in basic open hearth steel furnaces where a number of courses of magnesia brick are used in making the foundation for the bottom, the bottom being made of dead-burned magnesite, and in many cases at present, of granular dolomite. Side walls are built of magnesia brick to a height of about 15 inches above the bottom of the charging doors. They are used around the door jambs and tapping holes, and to face the furnace blocks as a protection to the silica bricks.

Magnesia bricks are used in the construction of soaking pits in the six or eight bottom courses; along the slag line of metal mixers; in the bottom and on the bridge wall of billet and bar heating furnaces; in the bottom side walls and bridge walls of copper reverberatories; in copper converters and special types of furnaces such as silver slimes, dross and bullion furnaces, electrical smelting, heating, welding and melting furnaces, calcium carbide kilns and other furnaces.

Previous Work

Many attempts have been made to obtain a dead burned dolomite but with varied success. There have been three general lines of procedure employed in these attempts which are as follows:

1. By mixing an impurity with finely ground dolomite and calcining the mixture.[1] The impurities used are: silica, iron oxide, roll scale, flue dust, alumina, chromium oxide, manganese oxide, cobalt oxide, nickel oxide, borax, blast furnace slag, basic open hearth slag, shale, kaolin, coal tar, calcium chloride, magnesium chloride and sodium chloride.

2. By mixing an impurity with coarsely ground dolomite (2–8 mesh) and calcining the mixture.[2] An example of this method is that used in recent times for making sinter dolomite by allowing the grains of dolomite to float about in a bath of molten iron, until the entire grain has encased

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[1] G. L. Davison, "Dead Burning Magnesite," U. S. 792,382 June 20 (1905); C. B. Stowe, "Dead Burning Magnesite," U. S. 205,056, Nov. 14 (1916); G. O. Handy and R. M. Isham, "Dead Burning Dolomite," U. S. 1,270,818, July 2 (1918); S. B. Newberry, "Dead Burning Dolomite," U. S. 1,267,686, May 28 (1918); H. G. Schurecht, "Experiments in Dead Burning Dolomite," *J. Am. Ceram. Soc.*, 2 [4], 291 (1919); A. Rollason, "Refractory Substances," Brit. 156,447, April 21 (1920); H. G. Schurecht, "Experiments in Dead Burning Dolomite and Magnesite," *J. Am. Ceram. Soc.*, **4** [2], 127 (1921); C. H. Breeswood, "Dolomite Bricks," U. S. 1,380,701, June 7 (1921).

[2] F. A. Jones, "Process of Producing a Furnace Lining with Dolomite," U. S. 151,535, Jan. 1 (1918); M. Backheuer, "The Preparation of the Dolomite-tar Mixture in Thomas (basic converter) Steel Works," *Stahl u. Eisen*, **41**, 954 (1921).

itself in a protective coating of iron. Also the present used methods for sintering coarse dolomite with basic open hearth slag or other flux come under this classification.

3. The third method used is to separate the MgO from dolomite ($MgCa(CO_3)_2$). It is much easier to dead burn MgO than CaO since CaO has a greater tendency to combine with water and slake, hence several methods have been proposed to extract the MgO from dolomite and use it as a refractory.[1]

This separation of MgO from CaO after calcining the dolomite at various temperatures is accomplished in several ways, such as by chemical-treatment, flotation, elutriation, leaching and screening.

There are also methods used where the dolomite is not previously calcined.[2]

The most promising and generally used methods for attempting to dead burn dolomite for brick purposes are those methods listed in section 1 where the finely ground dolomite is calcined together with a flux.

For dead burning dolomite in granular form, method 2 is in general use.

This grain dolomite is used for bottoms of basic open hearth furnaces and patching. Magnesite bricks are used for the foundation of the bottom and granular dolomite or magnesite for the remainder. When the dolomite is burned at the plant it may be mixed with slag and sintered into place in the same way as magnesite. When prepared dolomites are used, this latter step is sometimes unnecessary as they have the proper composition for setting. Analysis of some of these prepared dolomites are as follows:[3]

	SiO_2	Fe_2O_3-Al_2O_3	CaO	MgO	Mn	Ignition loss
Magdolite..............	5.77	6.12	51.05	35.05	n. d.[1]	0.82
Magnite..............	1.35	1.52	59.70	37.77	n. d.	.50
Madgebrent..........	1.84	8.17	56.86	31.26	0.20	.51
Dolite................	2.20	0.86	57.37	38.16	n. d.	.85
Syndolag.............	4.66	6.18	52.80	31.76	0.98	.51

[1] No determination.

The construction of a furnace bottom requires about 90 tons of grains and 25 tons of ground slag.

When a furnace is operated intermittently, especially with prolonged shut-downs, the use of dolomite in any great thickness is unwise because it will slake to a powder upon exposure to the atmosphere. Even treated dolomites slake rather easily.

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[1] R. Scherer, "Der Magnesit," *A. Hartleben's Verlag, Wien u. Leipsig,* **84,** 134, 135 (1908); J. A. Bradburn, "Process of Obtaining Magnesia," U. S. 1,156,662, Oct. 2 (1915); A. M. Mitchell, "Process for Obtaining Magnesium Oxide from Dolomites," U. S. 1,273,110, July 16 (1918)

[2] H. Scherer, *ibid.*, p. 134.

[3] H. E. Townsend, Report, *Elec. Fur. Assn.,* **79,** Oct. 6 (1920).

Schurecht[1] made a careful study of the effects of fine grinding and different calcination temperatures on dolomite using the following fluxes: flue dust, iron ore, basic open hearth slag, kaolin and roll scale. The dolomite was ground to 100-mesh and 40-mesh and calcined with the above fluxes at cones 14, 20 and 26, in a Hoskins carbon resistance furnace. The tendency to slake is measured by the tendency the body shows to increase in weight.

The results he obtained may be summarized as follows:

1. **Flue Dust and Dolomite.**—Grinding the dolomite to 100-mesh size before calcination decreased its tendency to slake over that of 8-mesh dolomite. Also, increasing the calcination temperature above cone 14 increased the tendency of the dolomite to slake. Increase of flux in 40-mesh dolomite decreased the tendency to slake up to an addition of 10%. Above 10% flux, the tendency to slake varied with different percentages of flux.

2. **Iron Ore and Dolomite.**—Fine grinding of the raw dolomite decreases the tendency to slake. Increasing the calcination temperature above cone 14 again increases the tendency of the dolomite to take up moisture and carbon dioxide. The increase in flux acts similar to flue dust as given in the foregoing paragraph.

3. **Basic Open Hearth Slag and Dolomite.**—A mixture of 8-mesh dolomite and basic open hearth slag increased in weight much more than a similar mixture with 100-mesh dolomite. Increasing the calcination temperature above cone 14 likewise increases the tendency of the body to increase in weight even to a greater extent than when flue dust and iron ore were used as fluxes. This is attributed to the fact that the lime and silica content of the slag forms unstable compounds with the CaO of the dolomite.

4. **Kaolin and Dolomite.**—As before, fine grinding of the raw dolomite increases the resistance to slaking. Also, an increase in calcination temperature above cone 14 increases the tendency of the calcine to increase in weight. This was more pronounced on the high fired specimens than with the corresponding iron ore and flue dust mixtures. Some of the mixtures made with 5 and 10% kaolin were still sound at the end of $2^1/_2$ years storage at room temperature. This is attributed to the comparatively high silica-alumina content which evidently forms hydraulic compounds with the lime, similar to those in Portland cement. Kaolin proved to be a very effective flux in dead burning dolomite, being much better than high iron fluxes, probably due to the fact that alumina and silica are better fluxes of CaO than iron oxide and hence leave less uncombined lime.

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[1] H. G. Schurecht, *op. cit.*, **4** [2], 127 (1921).

5. Roll Scale and Dolomite.—A mixture of 8-mesh dolomite and roll scale when calcined, increased in weight more than a mixture of 100-mesh dolomite and roll scale, as in the other cases cited. However, increasing the calcination temperature did not materially cause the product to increase in weight.

6. Chlorides and Dolomite.—Adding calcium chloride, magnesium chloride and sodium chloride individually to dolomite and calcining, decreased the tendency of the calcine to slake to only a very slight extent.

From the above combinations, the following conclusions are drawn:

(1) Grinding the raw material fine, *i. e.*, through a 100-mesh sieve, seems necessary to produce the best results.

(2) In most cases increasing the calcination temperature above cone 14 increases the tendency of the calcined dolomite mixtures to take up moisture and carbon dioxide and to disintegrate, due to the formation of free lime and hydraulic compounds which hydrate slowly in the open air.

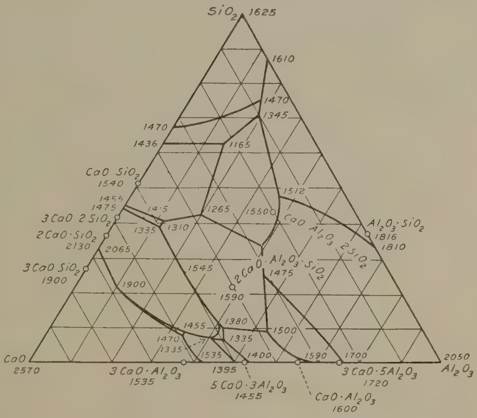

FIG. 1.—Ternary system $CaO–Al_2O_3–SiO_2$.

(3) Kaolin proved to be the most effective flux used for dead-burning dolomite.

Pyrochemical Behavior of Impurities Found in Dolomite

A review of the work carried on by the Geophysical Laboratory of Washington gives an idea of the pyrochemical behavior of the chief impurities found in dolomites.

The $CaO–Al_2O_3–SiO_2$ diagram as reported by G. A. Rankin,[1] is shown in Fig. 1. Here we have the compounds, $CaOSiO_2$, $3CaO2SiO_2$, $2CaOSiO_2$, $3CaOSiO_2$, $3CaOAl_2O_3$, $5CaO3Al_2O_3$, $CaOAl_2O_3$, $3CaO5Al_2O_3$ and Al_2O_3-SiO_2. These compounds are at a maximum temperature with eutectics at the points shown. The boundary curves limiting the fields for the stable existence of the compounds (monovariant systems) are also shown. The figures on the diagram denote the fusion points of these mixtures and compounds. Among the natural minerals are found the ternary compounds: anorthite, meionite, gehlenite and grossularite, all lime-silica-alumina minerals. Grossularite and meionite do not form by directly fusing together the pure oxides, but nevertheless exist in the natural minerals. By fusing together the three oxides CaO, Al_2O_3 and SiO_2, we may thus obtain, at least, two ternary compounds: anorthite ($CaOAl_2O_3$-$2SiO_2$) and gehlenite ($2CaOAl_2O_3SiO_2$) and the eight binary compounds shown on the diagram.

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[1] G. A. Rankin, *Am. J. Sci.*, 39, 25 (1915).

These compounds are all stable and hence if the free lime ordinarily formed when calcining dolomite can be put into combination as any of these forms, there will be little danger of the hydration of free lime. The chief undesirable constituent to avoid is the β orthosilicate which inverts into the stable fine powder γ orthosilicate as will be mentioned later. The β dicalcium silicate has an index of refraction equal to 1.645 ± 0.003, the index of γ dicalcium silicate is 1.654 ± 0.003. The birefringence is medium, about 0.015.

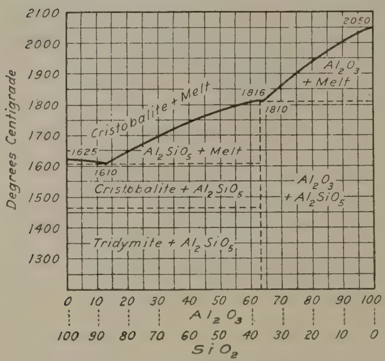

FIG. 2.—Binary system Al_2O_3–SiO_2. Weight, per cent.

The effect of alumina on silica is shown in Fig. 2. There is only one compound sillimanite, $Al_2O_3SiO_2$, which forms eutectics on either side of it. The eutectic between sillimanite and corundum occurs at 64% Al_2O_3 and 36% SiO_2 at a temperature slightly below the melting point of pure sillimanite, 1816°C. The eutectic between sillimanite and cristobalite occurs at 1610°C.

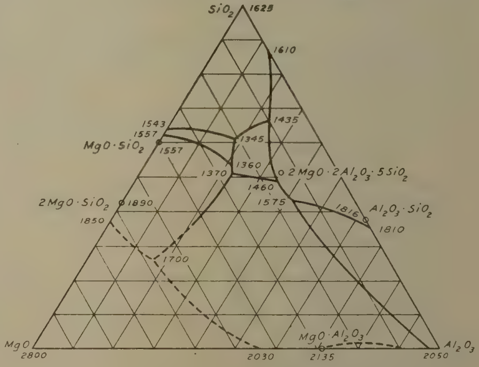

FIG. 3.—Ternary system MgO–Al_2O_3-SiO_2

The Ternary System MgO–Al_2O_3–SiO_2[1]

This system is shown in Fig. 3. Here we see that the binary compounds $2MgOSiO_2$ (forsterite), $MgOSiO_2$ (enstatite), $MgOAl_2O_3$ (spinel), $Al_2O_3SiO_2$ (sillimanite), and a ternary compound $2MgO2Al_2O_35SiO_2$ (cordierite) may form, which all have lower melting points than MgO itself besides various eutectics as shown in the triaxial.

The Ternary System CaO–MgO–SiO_2[2]

For this system see Fig. 4. Here the definite compounds α $CaOSiO_2$ (pseudowollastonite), $3CaO2SiO_2$, α and β $2CaOSiO_2$, $MgOSiO_2$ (clinoenstatite), $2MgOSiO_2$ (forsterite), $CaOMgO2SiO_2$ (diopside), 5CaO2MgO-$6SiO_2$ and $2CaOMgO2SiO_2$ (akermanite) have fusion temperatures as shown on the diagram.

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[1] Rankin & Merwin, *Am. J. Sci.*, **45**, 304 (1918).

[2] Ferguson & Merwin, *ibid.*, **48**, 109 (1919).

The System Anorthite–Forsterite–Silica[1]

This system is shown in Fig. 5. The general character of the true ternary part of the diagram is that of a system with no ternary compound and one binary compound, clinoenstatite $MgOSiO_2$ unstable at its melting point of 1557°C. There are two quintuple points. M is an alteration point between anorthite, forsterite and enstatite with a composition of SiO_2 54.20%, Al_2O_3 20.16%, MgO 14.59%, CaO 11.05% and with a melting point of 1260° ± 2°C. The ternary eutectic between anorthite and clinoenstatite and tridymite has a composition of SiO_2 61.90%, Al_2O_3 18.51%, CaO 10.15%, MgO 9.44% having a temperature of 1222° ± 2°C.

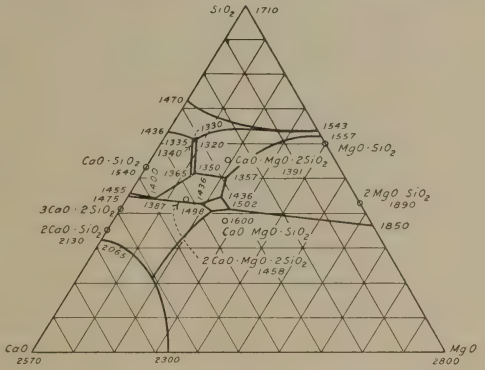

FIG. 4.—Ternary system $CaO–MgO–SiO_2$.

The Ternary System $CaO–Al_2O_3–MgO$.[2]

This system is shown in Fig. 6. As shown there is no ternary compound formed. There are six quintuple points of the following compositions and melting points:

Point				Melting point
1	CaO 51.5	Al_2O_3 42.3	MgO 6.2	1450° ± 5°
2	CaO 46.0	Al_2O_3 47.7	MgO 6.3	1345° ± 5°
3	CaO 41.5	Al_2O_3 51.8	MgO 6.7	1345° ± 5°
4	CaO 40.7	Al_2O_3 52.4	MgO 6.9	1370° ± 5°
5	CaO 33.3	Al_2O_3 63.2	MgO 3.5	1550° ± 5°
6	CaO 21.0	Al_2O_3 74.0	MgO 5.0	1680° ± 20°

Preliminary Report on the System Lime–Ferric Oxide[3]

Figure 7 shows the binary system lime–ferric oxide. There are only two calcium ferrites having the formula of the dicalcic ferrite ($2CaOFe_2O_3$) and the monocalcic ferrite ($CaOFe_2O_3$) with dissociation temperatures at 1436° and 1216°C, respectively.

---

[1] Olaf Anderson, *Am. J. Sci.*, **39**, 440 (1915).

[2] Rankin & Merwin, *J. Am. Chem. Soc.*, **38**, 575 (1916).

[3] Sosman and Merwin, *J. Wash. Acad. Sci.*, **6**, 532–7 (1916).

Campbell[1] shows that if a mixture of pure silica, ferric oxide and calcium oxide of the same molecular proportion as those found in the celite drawn off from Portland cement clinker, is melted and slowly cooled, large crystals of tricalcic silicate will separate, thus demonstrating that calcium ferrite may act as a solvent for both calcium silicate and lime, in a manner almost exactly similar to that of the calcium aluminate.[2]

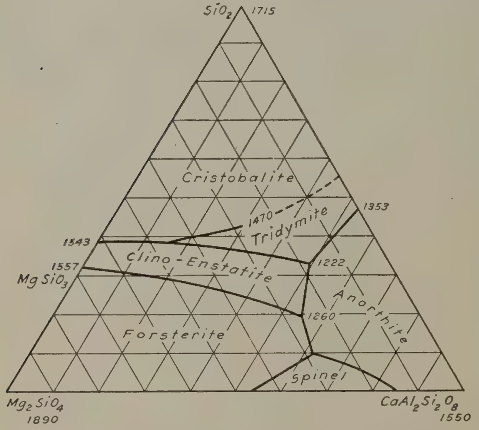

FIG. 5.—System anorthite–forsterite–silica.

CaO–MgO System[3]

Figure 8 shows the effect of lowering the melting point of MgO by the presence of CaO. In this system it was found that in all fused mixtures of CaO and MgO, the two oxides crystallize out side by side, showing no evidence of combination, that is, there is no stable compound formed. The eutectic formed has the approximate composition CaO 67%, MgO 33% and its melting point is 2300° ± 50° which, as seen from the other curves shown, is a higher fusion point than where Al_2O_3, Fe_2O_3 or SiO_2 are added to CaO or MgO.

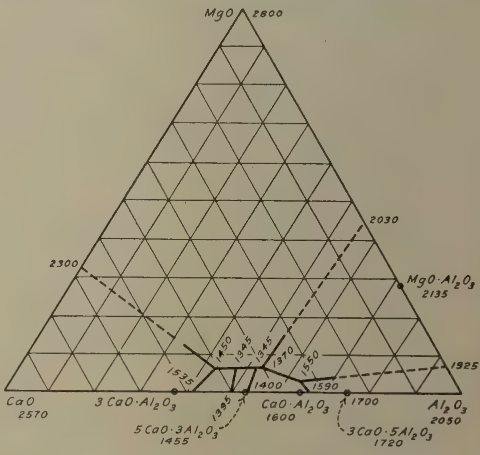

FIG. 6.—Ternary system CaO–Al_2O_3–MgO.

The effect of Al_2O_3 and SiO_2 on lowering the fusion temperature of CaO, MgO and CaO MgO (the theoretical ratio in which CaO and MgO exist in dolomite), as obtained from the previous curves is shown in Figs. 9 and 10. These curves show that SiO_2 has a much greater effect on lowering the fusion temperature of MgO than Al_2O_3 has. SiO_2 lowers the fusion temperature of CaO

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[1] Campbell, "Function of Ferric Oxide in the Formation of Portland Cement Clinker," *J. Ind. Eng. Chem.*, **7**, 835–7 (1915).

[2] H. A. Miers, *Mineralogy*, p. 385 (1902) states that iron oxide forms a spinel with Al_2O_3 of the formula $FeOAl_2O_3$ called hercynite.

[3] Rankin and Merwin, *J. Am. Chem. Soc.*, **38**, 571 (1916)

MgO more rapidly and to a lower temperature than does Al_2O_3. On the contrary Al_2O_3 lowers the fusion temperature of CaO more rapidly and to a greater extent than does SiO_2. The fusion temperature of CaO MgO with SiO_2 as a flux is lower than that of CaO or MgO alone with SiO_2 as a flux. In greater amounts than about 21% and less than about 83%, Al_2O_3 lowers the fusion temperature of pure CaO below that of CaO MgO.

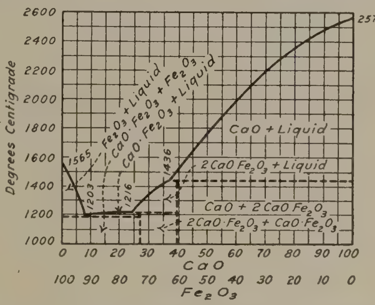

FIG. 7.—The binary system CaO–Fe_2O_3.

Schurecht[1] found that a large percentage of iron oxide 20–30% with 80–70% dolomite may be used without decreasing the refractoriness below cone 31. Impurities which are siliceous in character like kaolin, he found to decrease the refractoriness to a much greater extent. Work later on in this article will show that it was probably not the presence of silica which caused the decrease in refractoriness, but the presence of Al_2O_3 which caused the excessive lowering in the fusion temperature.

From these aforementioned diagrams and data we see that any of the following compounds may exist in dead-burned dolomite when Fe_2O_3, Al_2O_3 and SiO_2 are present:

CaO SiO_2—Wollastonite
3CaO $2SiO_2$
2CaO SiO_2—Calcium orthosilicate
3CaO SiO_2—Tricalcium silicate
CaO MgO SiO_2—Monticellite
CaO MgO $2SiO_2$—Diopside
2CaO MgO $2SiO_2$—Akermanite
5CaO 2MgO $6SiO_2$
3CaO Al_2O_3—Tricalcium aluminate
5CaO $3Al_2O_3$
CaO Al_2O_3—Calcium aluminate
3CaO $5Al_2O_3$
CaO Al_2O_3 $2SiO_2$—Anorthite
2CaO Al_2O_3 SiO_2—Gehlenite
MgO SiO_2—Enstatite
2MgO SiO_2—Forsterite
MgO Al_2O_3—Spinel
2MgO $2Al_2O_3$ $5SiO_2$—Cordierite
5CaO 2MgO $6SiO_2$
Al_2O_3 SiO_2—Sillimanite
2CaO Fe_2O_3—Dicalcic ferrite
CaO Fe_2O_3—Monocalcic ferrite

Since, as shown by these diagrams, the compounds and especially the eutectic mixtures have fusion points at relatively low temperatures, in all probability the amount of flux added to the dolomite will have to be limited to within a few per cent of the dolomite so as not to exercise too great an influence on the softening temperature of the mixture, thus destroying its value as a refractory.

Of course these diagrams represent equilibrium conditions, *i. e.*, that the compounds and components as represented would occur together in mixtures if time were allowed for the reaction to go to completion which most probably will not be the actual case when dolomite is calcined with fluxes. The diagrams show, however, what compounds may be formed in calcining such a mixture. They show that there are numerous possibilities in forming various eutectic mixtures and also stable compounds which may be formed by reaction of the fluxing oxides with CaO and MgO of the dolomite, or it is possible that a eutectic mixture or compound may be formed between all the oxides which will dissolve the excess CaO and MgO, thus producing a stable form. Absolutely dead-burned magnesite has the magnesite essentially in the form of periclase.[1] By adding fluxes to dolomite and calcining at a sufficiently high temperature, it may be possible to form the MgO into periclase and have the otherwise free lime, which would tend to slake, combine with the fluxes present to form stable compounds.

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[1] H. G. Schurecht, *J. Am. Ceram. Soc.*, **2** [4], 305 (1919).

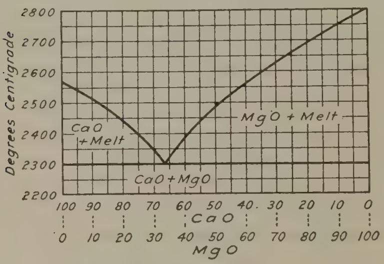

FIG. 8.—Binary system CaO–MgO.

Austrian magnesite, which dead burns to form the ordinary magnesia brick, is called Breunnerite, which is an isomorphous mixture of magnesium and iron carbonates. When this mineral is calcined and dead burned the resulting product takes on a yellowish tinge. This is due to the solution of the ferric oxide formed into the periclase formed. Adding iron oxide to a magnesite too low in the iron oxide content gives a satisfactory product.[2]

The composition of Breunnerite varies from 95–70% $MgCO_3$ and 5–30% $FeCO_3$.[3]

Pike[4] states that amorphous magnesite raised to a temperature of 1550°C in the presence of 5–6% Fe_2O_3 is transformed into periclase which is dense, hard and sintered and known as dead-burned magnesite. Microscopic examination demonstrates that Fe_2O_3 added to the rock under proper conditions is equivalent in action to the iron occurring naturally in the rock. The natural occurring

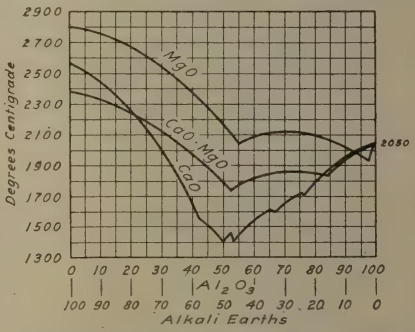

FIG. 9.—Effect of Al_2O_3 on the fusion of CaO, MgO and CaO. MgO.

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[1] J. S. McDowell and R. M. Howe, "Magnesite Refractories," *J. Am. Ceram. Soc.*, **3** [3], 211 (1920).

[2] J. S. McDowell and R. M. Howe, *loc. cit.*, **3** [3], 190–1 (1920).

[3] Thos. Crook, "Magnesite as Raw Material," *Trans. Ceram. Soc.* (Eng.), **18,** 75 (1918–19).

[4] R. D. Pike, "Electric Furnace Refractories," *Chem. Met. Eng.*, **23,** 1148 (1920).

crystalline Austrian magnesite or Breunnerite, however, is far superior to other forms of magnesite[1] and is the chief product used for making magnesia brick in the United States today. Since Breunnerite which contains iron carbonate, forms a better dead-burned product than crystalline Washington magnesite which is low in iron, and since a small percentage of iron oxide, 4.5–8.0%, is considered necessary for the production of dead-burned magnesite for refractory purposes,[2] it appears to be advisable to add it as one of the fluxes in dead-burning dolomite, since if a small percentage of ferric oxide is added to a pure dolomite, the two finely ground together and calcined at a high temperature, there is a tendency to approach the homogeneous composition of Breunnerite.

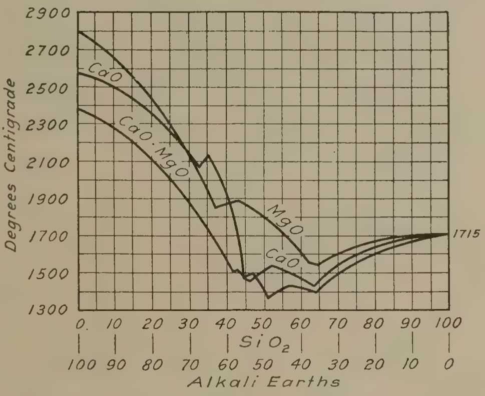

FIG. 10.—Effect of SiO_2 on the fusion of CaO, MgO and CaO . MgO.

The presence of impurities, especially silica and silicates, causes lime to be overburned. This appears to be true since it has been found practically impossible to overburn some very pure limes.[3] Overburned lime is generally yellow or black in color. It is very inactive to water and slakes not at all or very slowly. Thus the presence of silica or silicates when mixed with dolomite may tend to cause the lime to "overburn" when calcined.

Slaking of Dolomite

The disintegration of dolomite is due to the two following causes:

1. Disintegration due to change of state on heating and cooling.
2. Disintegration due to slaking by taking up moisture from the air.

In the first case the disintegration is comparatively rapid occurring during the cooling and is due to the inversion from the β to γ form of orthosilicate which starts at about 675°C[4] and continues even after it is removed from the furnace. This inversion is accompanied by a 10% volume change which causes dusting of the orthosilicate and the dolomite containing it. Newberry, Richardson, Boudouard and Le Chatelier[1] all noticed this dusting and Le Chatelier ascribed it properly as being due to polymorphism. Schurecht[2] found that blast furnace slag used as a flux for dolomite caused considerable dusting due to this conversion of β $2CaOSiO_2$ to γ $2CaOSiO_2$. This was caused by the high SiO_2 content of the flux. He noticed this dusting to a less extent when flue dust, kaolin or basic open hearth slag were used and mixtures containing roll scale or iron ore showed the least dusting as would be expected. Bates[3] showed that in Portland cement containing above 4.5% MgO, the rapidity and amount of dusting increases with the magnesia content up to about 9.5% MgO content when the orthosilicate begins to decrease again with addition of MgO.

---

[1] A. F. Greaves-Walker, "Electric Furnace Refractories," *Elec. Fur. Assn.*, **57**, Oct. 6 (1920).

[2] McDowell and Howe, *loc. cit.*, **3** [3], 203 (1920).

[3] W. E. Emley, U. S. Bur. Stand., *Tech. Paper* **16** (1913).

[4] Shepard and Rankin, "Preliminary Report on the Ternary System CaO–Al_2O_3–SiO_2," *J. Ind. Eng. Chem.*, **3**, 9 (1911).

Disintegration due to taking up moisture from the air is due primarily to the presence of free lime in the calcined material which takes up water and forms calcium hydroxide according to the simple chemical equation

$$CaO + HOH \longrightarrow Ca(OH)_2.$$

This is purely a case of lime slaking where the increased volume of the $Ca(OH)_2$ disrupts the mass causing it to slake down into powder. As a secondary reaction we have

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O.$$

Davis[4] shows that "underburned" cement contains a considerable quantity of free lime. Cements such as this when mixed with water set rapidly. The particles of free lime absorb moisture changing to the hydrate of lime and the expansion which accompanies this change produces ominous cracks in the hardened cement.

This disintegration, due to the taking up of moisture, may also be due to various compounds formed in the calcine which possess hydraulic properties and in taking up water from the air, cause the calcined material to disintegrate. Klein and Phillips[5] found that the following compounds will hydrate: $3CaO\ Al_2O_3$, $5CaO\ 3Al_2O_3$, $CaO\ Al_2O_3$, $3CaO\ SiO_2$ and $\beta\ 2CaOSiO_2$. They found that $CaO\ SiO_2$ and $\gamma\ 2CaO\ SiO_2$ do not possess hydraulic properties. Campbell[6] showed that the two ferrites of calcium, monocalcic ferrite and dicalcic ferrite will hydrate also. Magnesium oxide will combine with water with reasonable rapidity, only when it has been burned at some temperature below 1100°C. It may be that these compounds, if present in sintered dolomite, will, during the process of their hydration, cause a volume change and cause the calcined dolomite to disintegrate. Schurecht's work showed that compounds having a tendency to increase in weight when exposed to the air are formed in dolomite calcined with various fluxes. Bates[1] shows that Portland cement high in magnesia produces concrete similar, so far as expansion is concerned, to concrete made from the normal composition. This cement shows usually contraction when stored in air and expansion when stored in water. The expansion and contraction of these compounds, however, is only very slight, in most cases not more than a few hundredths of one per cent. A large part of the magnesium does not hydrate, it acts merely as an inert substance which must be heated by the calcium oxide. Therefore, other things being equal, the less magnesium oxide present in a lime, the more quickly will it slake and the greater will be the amount of heat generated. However, a very porous dolomitic lime may slake more quickly than a dense lime with a much higher content of calcium oxide, due to the fact that the water can penetrate the more porous lime more quickly. Evidently it appears that in order to dead burn dolomite, a dolomite of as high MgO content as possible is desirable and as previously mentioned, a fine grained material is desirable in order to develop a dense product.

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[1] Newberry, *J. Soc. Chem. Ind.*, **16,** 887 (1897); Richardson, *Cement,* **4,** 276 (1903); Boudouard, *Rev. de Metal,* 462 (1905); LeChatelier, *Ann. d. Mines,* 345 (1887).

[2] H. G. Schurecht, *J. Am. Ceram. Soc.*, **2** [4], 304 (1919).

[3] P. H. Bates, "Properties of Portland Cement having a High Magnesia Content," U. S. Bur. Stand., *Tech. Paper* **102,** 40 (1918).

[4] A. C. Davis, *Port. Cement,* **22** (1909).

[5] Klein and Phillips, "The Hydration of Portland Cement," *Trans. Am. Ceram. Soc.*, **16,** 313–41 (1914).

[6] E. D. Campbell, *J. Ind. Eng. Chem.*, **11,** 116–20 (1919).

Summary

Thus it has been shown that:

1. Kaolin appears to be a fairly effective flux for dead-burning dolomite.
2. There are many different compounds and eutectic mixtures capable of formation among the five components CaO, MgO, Fe_2O_3, Al_2O_3, and SiO_2.
3. CaO may combine with Fe_2O_3 and act as a solvent for lime as does also calcium aluminate.
4. The presence of Fe_2O_3 is essential to dead burn MgO to the stable form periclase.
5. Lime is rendered inactive to water by calcination in the presence of impurities especially silica and silicates.
6. The more magnesium oxide present in a lime, the slower will it slake.

In view of these facts it was deemed advisable to carry on this investigation of determining whether or not it is possible to dead burn dolomite using Fe_2O_3, Al_2O_3 and SiO_2 either alone, a combination of any two, or a combination of all three as fluxes.

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[1] P. H. Bates, *op. cit.*, 21–4.

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ORIGINAL PAPERS

THE BONDING EFFECT OF BALL CLAYS IN FIRED BODIES[1]

BY H. H. SORTWELL

ABSTRACT

Seven American and fourteen English ball clays were compared in regard to bonding effect, (*a*) after burning, in a composition containing no fluxes, at cones 5, 8, 10 and 12; (*b*) in a semi-porcelain body burned to cone 8; and (*c*) in a vitreous china body burned to cone 11. The English clays developed greater strength in the absence of fluxes. The semi-porcelain and vitreous china bodies containing the imported clays were in general of greater strength than those bodies in which the domestic clays were used, but most of the bodies containing American clays were of good transverse strength.

Introduction

Ball clay, because of its property of burning to a strong, dense structure at temperatures used in maturing chinaware, imparts strength to the product in addition to that produced through the action of fluxes. Since the mechanical strength of this type of ware is of great importance, it is desirable to know the relative effects of various ball clays, and the present investigation was undertaken to obtain this data.

This investigation is a continuation of the work reported in the Bureau of Standards, *Technologic Paper* No. 227, which deals with the physical characteristics and the drying and burning behavior of ball clays. The clays used in this study are a part of the same shipments used in the previous investigation. The data in this report are, therefore, comparable with those given in the *Technologic Paper* mentioned and the moduli of rupture of the clays in the dry state, as given, are quoted from that paper.

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[1] Published by permission of the Director of the Bureau of Standards of the U. S. Department of Commerce. Received Dec. 1, 1923.

Procedure

The seven American and fourteen English ball clays used in the investigation were compared with regard to bonding effect in burned bodies in: (*a*) A composition containing no fluxes and burned to cones 5, 8, 10 and 12; (*b*) A semi-porcelain body burned to cone 8; and (*c*) A vitreous body burned to cone 11. Orton pyrometric cones were used in this work.

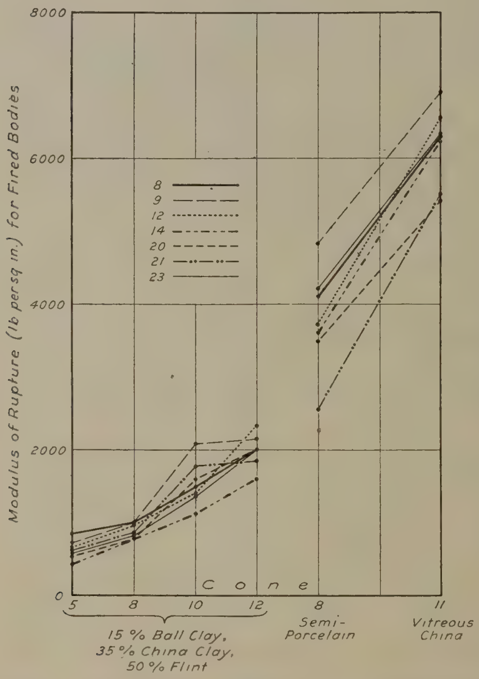

FIG. 1.—Transverse strength of compositions containing American ball clays.

The moisture content of the clays was determined so that comparisons could be made on the basis of the dry material. Each of the mixtures was ground in a ball mill two hours, filter-pressed, wedged, and pressed into bars 6 by 1 by 1 inches. Fifteen bars were made from each batch for each firing treatment.

For the comparison of the bonding effect of the clays in the absence of fluxes, the following composition was used with each clay: 50% flint, 35% English china clay, 15% ball clay.

Specimens of these compositions were fired at cones 5, 8, 10 and 12.

The semi-porcelain and vitreous china compositions used were:

	Semi-porcelain, per cent
Ball clay	15
Florida kaolin	8
English china clay	29
Maine feldspar	14
Flint	34

	Vitreous china, per cent
Ball clay	7 1/2
Florida kaolin	8
English china clay	29
Maine feldspar	18
Flint	36
Whiting	1 1/2

The semi-porcelain bodies were fired to cone 8 and the china bodies at cone 11.

All of the firing was done in a natural draft gas-fired laboratory kiln of the Bureau. The kiln was heated to 1000°C in fifteen hours and was finished at the cone desired in about fifteen hours more. Cones were placed in each sagger and showed a variation of less than half a cone throughout the kiln for each burn. Specimens of each composition were distributed in various saggers throughout the kiln in order that possible variations in firing would affect equally all of the bodies.

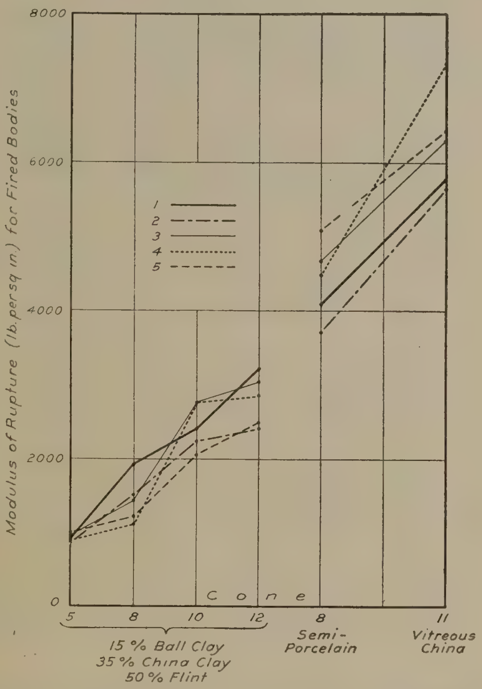

FIG. 2.—Transverse strength of compositions containing English ball clays.

The fired bars were broken over a five-inch span in an Olsen transverse testing machine of 1000 pounds capacity and the moduli of rupture computed. The amount of absorption of the semi-porcelain and china bodies was determined by the following method, which corresponds more closely to pottery practice than does the use of a vacuum.

The specimens were dried to constant weight at 110°C. They were then immersed in boiling water for five hours and allowed to cool to room temperature. When cool, the specimens were dried lightly with a damp cloth to remove excess water, and weighed in air. The per cent absorption was then calculated according to the following formula:

$$\text{Per cent absorption} = \frac{\text{wet weight} - \text{dry weight}\,.100}{\text{dry weight}}$$

Results

All of the numerical results given in Table I are the averages of five determinations. Fig. 1 shows graphically the transverse strength of the domestic clays tested in the fired compositions and corresponding data for the imported clays are given in Figs. 2, 3 and 4. The transverse strengths of the dried bodies are shown in Fig. 5.

Bodies Containing No Fluxes

A study of the strengths of fired compositions containing no feldspar indicates the differences in bonding power of the clays when no flux is present. The following Table II shows clearly the comparison of the American and English clays:

TABLE II

	American clays, range in strength	Average	English clays, range in strength	Average
Cone 5	439 to 845	633	885 to 1333	1032
Cone 8	810 to 1004	891	1077 to 1926	1542
Cone 10	1121 to 2135	1574	1572 to 2905	2442
Cone 12	1620 to 2355	1999	2467 to 3360	2980

In general, the dense burning English ball clays develop much greater strength in bodies containing no fluxes than do the American ball clays which do not vitrify at pottery temperatures. Consequently, the former are more desirable for use in those compositions in which clays alone are relied upon to produce high strength.

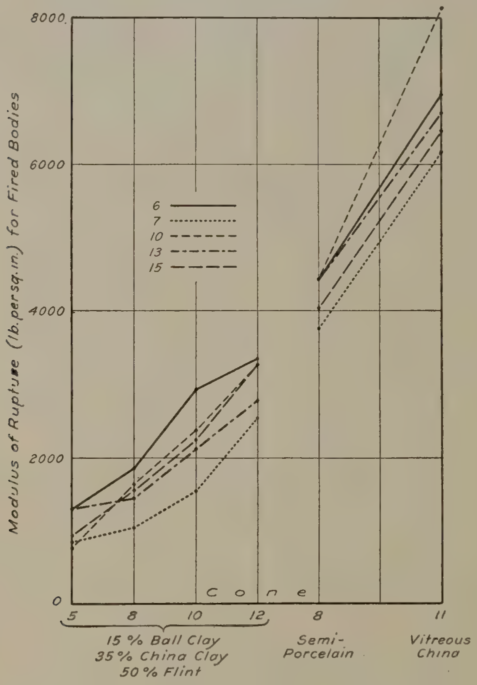

FIG. 3.—Transverse strength of compositions containing English ball clays.

From a comparison of the transverse strength of these bodies with those of the dried clay-flint mixtures it is apparent that the latter do not give a reliable indication of the bonding effect after firing.

Semi-Porcelain Bodies

The moduli of rupture of the semi-porcelain bodies varied from 3500 to 5000 pounds per square inch, with the exception of body No. 21, which developed a strength of 2560 pounds per square inch. From these data it is evident that ball clays greatly affect the strength of this type of body when burned.

The difference in bonding effect between the domestic and imported clays was not so pronounced in the semi-porcelain body containing 14% of feldspar as in the bodies containing no fluxes. Several of the semi-porcelains made with American clays were of good strength, the moduli of rupture of the bodies, with one exception, varying from 3500 to 4854 pounds per square inch, and averaging 4034 pounds. The same type of body, using English ball clays, ranged from 3783 to 5055 pounds per square inch, and averaged 4312 pounds.

TABLE I

RESULTS OF MODULUS OF RUPTURE AND ABSORPTION DETERMINATIONS

Lab. No.	Name of clay	Modulus of rupture dried 50 clay—50 flint	Modulus of rupture Cone 5	Modulus of rupture Cone 8	Modulus of rupture Cone 10	Modulus of rupture Cone 12	Semi-porcelain		Vitreous china	
							Modulus of rupture Cone 8	Per cent absorption Cone 8	Modulus of rupture Cone 11	Per cent absorption Cone 11
1	English ball clay No. 1	376	958	1926	2473	3271	4108	11.8	5869	2.0
2	English ball clay No. 2	375	937	1527	2300	2467	3783	11.3	5694	2.9
3	English ball clay No. 12	568	1085	1424	2730	3066	4687	9.1	6385	1.3
4	Whiteway ball clay	446	911	1178	2744	2898	4470	9.5	7411	.5
5	English ball clay No. 90	441	1059	1256	2095	2533	5055	8.8	6445	2.2
6	Pikes ball clay	381	1331	1872	2905	3360	4387	7.2	7023	.9
7	Superior ball clay	563	885	1077	1572	2561	3788	8.9	6188	1.6
8	Kentucky ball clay No. 4	372	845	999	1513	1982	4118	9.9	6333	1.7
9	Tennessee ball clay No. 5	478	702	947	2135	2104	4854	8.4	6922	1.2
10	No. 25 blue ball clay	403	868	1673	2375	3297	4361	9.5	8114	.9
12	Tennessee ball clay No. 11	293	682	1004	1447	2355	3748	12.1	6563	.6
13	Dorset ball clay	492	1333	1502	2184	2844	4396	10.5	6734	.9
14	Kentucky ball clay No. 10	223	439	844	1121	1620	3671	11.6	6226	1.4
15	English ball clay No. 11	396	1002	1668	2290	3332	4031	10.0	6505	.9
16	Fayles ball clay	347	1169	1664	2798	2871	4207	9.5	6545	.8
17	Grindley ball clay	427	913	1320	2518	3207	4568	9.3	6072	1.4
18	Great Beam ball clay	454	1011	1649	2682	3207	4335	10.9	5950	1.4
20	Tennessee ball clay No. 3	327	554	811	1576	1992	3500	11.9	5443	3.9
21	Tennessee ball clay No. 10	. . .	587	825	1785	1893	2564	13.8	5583	1.7
22	M. & M. English ball clay	384	994	1857	2558	2800	4194	10.7	5502	3.0
23	Tennessee ball clay No. 9	. . .	625	810	1440	2048	4212	10.6	6430	2.9

It is interesting to note, in this connection, that the bonding effect of the ball clays in the semi-porcelain bodies appears in some instances to be related to the bonding effect in bodies containing no fluxes. However, this relation is not dependable and the bonding power of a ball clay should, therefore, be studied in the type of body in which it is to be used.

The effect of the ball clay on the absorption is shown in Table I. The semi-porcelains varied from 7.2% in the case of No. 6, an English clay, to 13.8% in the case of No. 21, the clay which developed the least strength of all of the bodies at cone 8. However, a small part of this difference must be attributed to slight variations in firing.

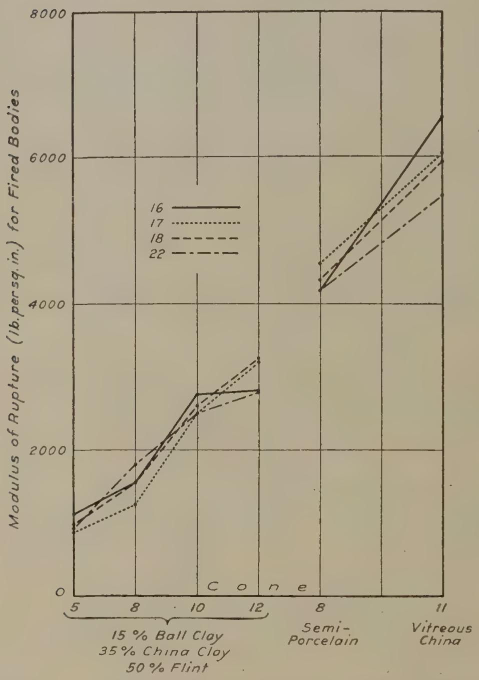

FIG. 4.—Transverse strength of compositions containing English ball clays.

Vitreous Bodies

In regard to the relative values for domestic and foreign clays, the results on the vitreous china compositions containing only $7^1/_2$% of ball clay were similar to those for the semi-porcelains. The bodies containing domestic ball clays had moduli of rupture ranging from 5443 to 6922 pounds per square inch, while those with imported clays ranged from 5502 to 8114 pounds per square inch. The averages were 6214 for the domestic clays and 6460 for the English.

A special body of this type, containing English china clay instead of ball clay, was prepared and burned. This body developed a modulus of rupture of 5875 pounds per square inch, which was higher than that of several of the bodies containing ball clays. This might indicate that some of the ball clays had been fired higher than the temperature at which their maximum strength is developed.

General

Neither the strength in the dried state nor the strength in bodies containing no fluxes gives dependable indication of the bonding effect to be expected in commercial semi-porcelain or vitreous compositions. For a reliable criterion of the strength of a body containing a given clay, the clay should be tested in the same composition and under same conditions of burning which are to be used in actual practice.

The difference in strength of the semi-porcelains and vitreous china composition bodies differing only in ball clay shows the important influence of the ball clay on the strength of the product and proves the value of a test of this kind in the selection of materials when developing compositions of high strength.

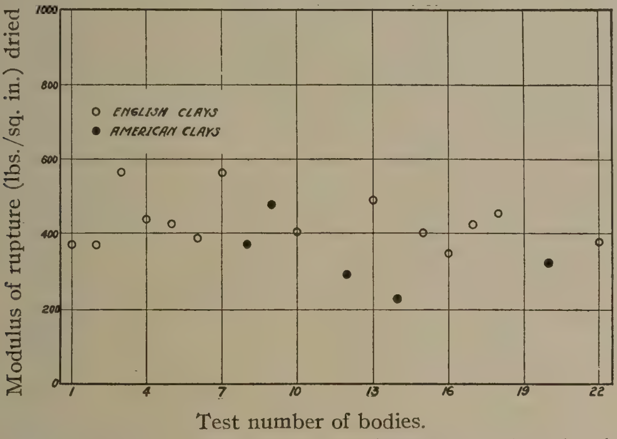

FIG. 5.—Strengths of American and English ball clays in the dried state.

Summary

Transverse strength determinations showed the fourteen English ball clays to have greater bonding effect, in general, than the seven American clays included in the work when used in a composition containing no fluxes.

The average strength of the semi-porcelain and vitreous china bodies containing the English ball clays was slightly higher than the same bodies containing the domestic ball clays. A number of the domestic clays, however, contributed greater strength to these bodies than the lowest imported clays, with results that were very satisfactory. Only three of the English clays gave extremely high strengths to the semi-porcelain and vitreous bodies.

Neither the strength of a clay in the dried state nor in a composition containing no active fluxes gave a reliable criterion of the strength to be contributed by it to a commercial composition.

The ball clay has an important effect on the mechanical strength of fired bodies, which should be taken into consideration in developing compositions of high strength.

U. S. BUREAU OF STANDARDS
WASHINGTON, D. C.

HANDLING AND STORING RAW MATERIALS TO PRODUCE UNIFORMITY IN A BODY[1]

By Robert Twells, Jr.

ABSTRACT

Ceramic raw materials are usually heterogeneous mixtures rather than pure substances. Variations in composition are likely to occur in the materials as received at the plant both within individual carloads and between successive carloads of the same material. Such variations often cause trouble in plants making vitreous porcelain. The article describes ways of avoiding trouble, (*a*) by rendering each carload homogeneous as it is stored, (*b*) by withdrawing a material from several lots simultaneously to make the body; in withdrawing from several lots simultaneously, the process should preferably be continuous, one lot being finished as a new one is started, (*d*) and by keeping accurate records of the materials going into each production batch of body.

As a rule the raw materials used in the ceramic industries are not pure substances. They consist usually of heterogeneous mixtures of minerals in different states of aggregation. Due to this inherent nature wide variations are likely to occur in their chemical and physical properties. These differences are relatively unimportant in some branches of ceramic work, but in the manufacture of vitreous ware, particularly high-fire vitreous ware, they are very important. Consequently in these industries a great deal of trouble and expense in handling is justified if it tends to insure uniformity in the raw materials.

If the materials are received at a plant in carload lots, variations usually occur in two ways:

(1) The first type is that found within an individual car. A sample from one part of a car may differ widely in chemical analysis and physical tests from another sample taken near by. Even a carefully selected average sample of an entire carload is not necessarily a safe guide for its use in production until the whole is rendered homogeneous. This can only be made certain by mixing the material thoroughly as it is being unloaded and stored. The amount of mixing necessary depends entirely upon the sensitiveness of the body to changes in the raw materials. For practical purposes it is usually sufficient to unload both ends of a car simultaneously and dump the materials together in a bin, preferably in the form of a cone. Finely ground materials in bulk are particularly adapted to this way of unloading as they are relatively well mixed as received, and when dumped in a pile are inclined to flow in all directions. Lump materials such as clays should also be unloaded simultaneously from both ends of the car but should be pulverized in a crusher before they are stored to prevent segregation of the different sizes. With a particularly sensitive body it might even be desirable to pass each material through a mechanical mixer before storing it in a bin. In any case each opportunity should be

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[1] A contribution from the Research Laboratories of the Champion Porcelain Company and the Jeffery-Dewitt Insulator Company. Received Dec. 19, 1923.

seized to mix a material as much as possible as it is being handled in order to make each carload as nearly homogeneous as practical.

(2) A second type of variation is that found between successive carloads of the same material. For example, a carefully taken average sample from one car usually differs considerably from a similar sample out of the next shipment. The problem in this case is to eliminate the differences between cars entirely or to lessen the danger of a change by making it occur more gradually. In contending with this type of variation there are several rules which, when observed, tend to eliminate possible difficulties:

(*a*) Each carload of material should be rendered homogeneous.

(*b*) As many carloads as practical of a material should be withdrawn simultaneously to make the body. This tends to counteract differences between individual carloads.

(*c*) As far as possible when drawing from several cars of a material it should be arranged that all the cars would not be finished at once, but one would be finished as a new one is started. In other words the system of storing and withdrawing should be continuous.

(*d*) It is often not convenient to store an individual carload of a material separately. When several carloads are dumped into one bin or pile the above rules should still be followed.

(*e*) Careful records should be kept of the materials going into each production batch of a body. Any changes in raw materials can then be traced through production and the effects noted. Trouble can often be avoided by knowing just at what point a change in the body is to be expected. Operating conditions can then be altered to correct for the differences.

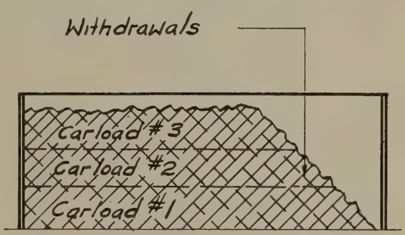


FIG. 1.—Sketch showing the method of storing three cars of a material in a bin and the method of withdrawal to produce a mixture of the three.

At the Champion Porcelain Company the above principles have been observed for some time in handling various quantities of new materials and also large amounts of scrap materials, kept for reuse. The particular methods followed may be of interest. The storage bins now in use each hold from two to three carloads depending on the size of the cars and the kind of material. The first carload (Fig. 1) is dumped into a bin roughly in the form of a cone or pyramid. It is then carefully leveled off to a uniform depth over the whole bin. A second car is likewise dumped on top of the first and leveled up in a similar manner. If the bin will hold a third car, it also is put in and leveled up like the first two. The result is that the bin contains two or three horizontal strata of material, each stratum being practically homogeneous. The material is withdrawn nearly vertically from one end of the bin giving practically a uniform mixture of all the cars for use in the body. This method eliminates the effects of variations between individual carloads but does not eliminate the possible result of a change from one bin to the next. To make the system continuous a slightly different plan has been used. One or more cars of a material are stored to a bin as described above. Three such bins of material are needed (Fig. 2.) One of the bins is used in the body until it is one-third empty; then a second bin is started and the two used in equal proportions until the first is two-thirds empty and the second one-third empty. The third bin is next started and the three used in equal parts until the first bin is empty, the second one-third full and the third two-thirds full. The first bin is then refilled and the three used in equal proportions, as before, each bin being refilled in turn as it becomes empty. This method can be extended to the mixing of as many separate bins as desired, but three are about its limit of practicability.

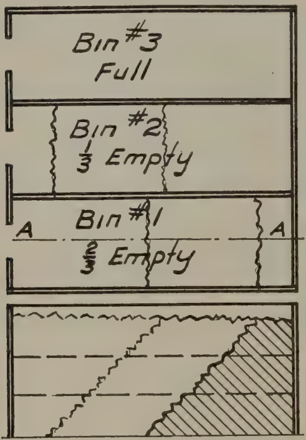
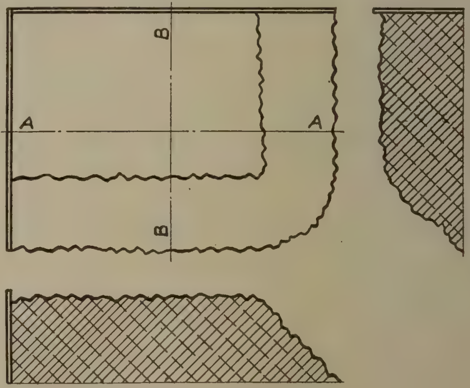


FIG. 2.—Sketch showing a continuous method of storing and withdrawing a material to produce a mixture of three bins, each bin holding three cars when full. The material is taken from the bins in equal proportions, and the bins are refilled as they are emptied.

For materials requiring great care it is desirable to mix as much as practical together in one large pile. For this purpose another plan has been successfully used in storing and mixing quantities up to a thousand tons. The pile (Fig. 3) is started at one end of an area and the material deposited in thin semi-vertical layers parallel to the first portion of the pile laid down. The pile can be extended in this way to any length desired.



SECTION B-B.—Dotted lines indicate method of withdrawal.

SECTION A-A.—Dotted lines indicate method of laying pile.

FIG. 3.—Sketch showing a method of storing a great many car loads of a material and the manner of withdrawal to produce a mixture of them all.

In withdrawing the material for use thin strips are removed from the entire face of the pile. These strips are taken at right angles to the original strata of the pile as laid down. Each layer withdrawn thus, contains a small amount of each stratum in the pile. This method as described is not continuous in operation. It can be made so by the continued deposition of new strata at one end of the pile, and the withdrawal of the material at the other end and a side at about a 60° angle with the original layers.

Some no doubt will feel that these precautions in handling raw materials are rather far-fetched and unnecessary. Whether or not similar methods would be advantageous in other ceramic industries is a question to be decided by the individual requirements. The writer believes that they are applicable generally in plants making products having close limits as to dimensions or using a body with a narrow firing range. Their adoption here was due to hard knocks previously received, and the results to date have been well worth the trouble. The present tendency at this plant is towards still greater care. Larger and larger amounts of material are being stored and increasing pains are being taken to render each practically homogeneous.

THE ELECTRICAL CONDUCTIVITY OF SODIUM CHLORIDE IN MOLTEN GLASS[1]

By Willard J. Sutton[2] and Alexander Silverman

ABSTRACT

Precipitation of collodial suspensions in glass by dissolved salts leads to the assumption that they ionize. In this investigation the conductivity of glass alone and with dissolved salts confirms the theory. A special cell has been devised for conductivity work in glass at high temperatures. This is the first study of the electrical conductivity of salts in vitreous media.

Introduction

This investigation was undertaken primarily to show that sodium chloride ionizes in molten glass as it does in aqueous solution, and also when the pure salt is heated to temperatures at or above its melting point. This was prompted by the tendency of chlorides and sulfates, dissolved in molten opal glasses, to precipitate the colloidal material, and produce alabaster glass through the destruction of opalescence.[3] The electrical conductivity of a simple soda-lime glass was first determined at various temperatures above the softening point, and then the conductivity was determined when the glass contained various percentages of sodium chloride.

There is but little data at present to show the molecular constitution of a glass. Conductivity measurements of molten salts have done much to show their degree of ionization, and molecular state. Since glass is but a supercooled liquid mixture of complex salts, conductivity data will most probably do much to solve this difficult problem of structure.

Historical Review

Considerable data have been obtained on the electrical conductivity of solid glasses of different types,[4] but only a little information is available for molten glass. This is due to the greater difficulty of measuring the conductivity of a molten glass, and because much of the work done on solid glasses was a study of electric insulators.

Glass has always been regarded as an electric insulator at room temperature, but as early as 1854 it was shown to be a conductor when heated to 100°C.[5] Warburg,[6] using voltages as high as sixty, and passing the

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[1] Contribution from the Department of Chemistry, University of Pittsburgh.

[2] Thesis submitted to the Faculty of the Graduate School, University of Pittsburgh, in partial fulfillment of requirements for the Ph.D. degree. Received Dec. 21, 1923.

[3] A. Silverman, *Jour. Amer. Ceram. Soc.*, **1,** 251 (1918).

[4] Clark, *Glass Ind.*, **2,** 221 (1921); "Smithsonian Physical Tables," 6th ed., 282 (1918); Gray and Dobbie, *Proc. Roy. Soc. London*, **67,** 197–200 (1900).

[5] Buff, *Liebig Ann.*, **90,** 257 (1854); Beetz, *ibid.*, **92,** 452 (1854).

[6] *Ann. Physik.*, **21,** 622 (1884).

current through a glass tube by means of mercury electrodes, found that the resistance of the glass increased quite rapidly, so that the current fell to a thousandth of its original value. With such high voltages, the resistance could not be due to polarization, and Warburg found sodium from the glass in the cathode mercury. A white, poorly conducting layer was formed in the glass at the anode surface. By using sodium amalgam as an anode, the current flowed through the glass without change or the formation of a poorly conducting layer, the sodium in the glass being constantly replaced as it was removed by electrolysis. By using lithium amalgam, Tegetmeier[1] showed that lithium could displace the sodium and be passed through the glass. The progress of the lithium into the glass could be measured as it formed a white opaque layer. Kraus and Darby[2] have shown that this can take place slowly without influence of the electric current, and that the white appearance was due to microscopic cracks, which in some cases caused the glass to disintegrate.

Warburg (*loc. cit.*), LeBlanc and Kerschbaum[3] and others have shown that the conduction of electricity through a glass obeys Faraday's law, but that only the positive alkali metal ions take part in the conduction. This condition, where solids conduct electricity, obeying Faraday's law, and where the positive ions carry all the current while the negative ions form a mechanically rigid framework, has been observed with silver chloride, silver bromide, silver iodide, silver sulfide (above 179 °C), and cuprous sulfide. In lead chloride and fluoride the negative ions carry the current.[4]

By passing a current through glass plates, LeBlanc and Kerschbaum produced poorly conducting layers at the anode surface, and on grinding these off, the glass conducted as well as before. A Thuringian glass containing approximately 9% of sodium was used, and when the current was reversed the conductivity would increase again almost to its original value. These investigators reasoned that the negative ions must have a composition $2(SiO_3 + xSiO_2)$ which should decompose to form $2(x + 1)SiO_2 + O_2$ in the poorly conducting layer. At the temperature used (250–300 °C) no gas was liberated, but on heating to higher temperatures oxygen was given off, chemically equivalent to the sodium found in the cathode mercury within the limits of experimental error.

By measuring the percentage of the sodium that can be removed from a glass by electrolysis, the fractional part which ionizes can be determined. LeBlanc and Kerschbaum found their glass to be 80% ionized. Kraus and Darby used a glass containing 16.90% Na_2O, 2.35% Fe_2O_3 and Al_2O_3, and 11.24% CaO and PbO. Data obtained on this glass are as follows:

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[1] *Ann. Physik.*, **41,** 18 (1890).

[2] *Jour. Amer. Chem. Soc.*, **44,** 2785 (1922).

[3] *Z. physik. Chem.*, **72,** 468 (1910).

[4] Tubandt, *Z. anorg. allgem. Chem.*, **115,** 105–126 (1921).

TABLE I

Temperature	278°C	295°	323°	343°
Ionization of sodium	74.4%	76.8%	79.4%	81.0%
Speed of sodium ion (cm./sec./v.)	4.52×10^{-8}	1.46×10^{-7}	3.26×10^{-7}	5.9×10^{-6}
Resistance, ohms	72,800	35,000	14,200	6,600

Heydweiller and Kopferman[1] and Kraus and Darby[2] have carried out the electrolysis of glass using molten salts as anodes. Lithium, sodium, potassium and silver can be readily introduced into the glass in this way, but the same change takes place slowly at high temperatures without the influence of the electric current. When sodium is displaced by other metals, the glass tends to crack on cooling. Copper, zinc, lead and other metals also enter glass when their molten salts are used as anodes, showing their entry by color effects, or disintegration. Silver had been found to be the best metal to replace sodium in glass, atom for atom, electrolytically. The speed of the ions could be measured by the moving boundary method, as the silver formed a light amber color at 250°C, which turned red or brown at higher temperatures.

When an ordinary soda lime glass is subjected to electrolysis at high temperatures, with concentrated sulfuric acid as an anode, the effect is similar to that mentioned when lithium amalgam was used.[3] The glass became opaque and white, and the current finally became greater than its original value. With Jena and lead glasses, however, a poorly conducting layer was formed.

Foussereau[4] has shown that a glass conducts better when tempered than when it is annealed. A certain lime glass decreased in conductivity 2.3 times on reheating and annealing. Gray and Dobbie (*loc. cit.*) determined the resistance of a potash lead glass at 130°C as $18{,}000 \times 10^{10}$ ohms. They found the resistance of a similar soda glass to be only 136×10^{10} ohms. Since the conduction is by the positive ions in solid glass, it is apparent that the specific conductivity is proportional to the absolute velocity of the ions present.

Porcelain is somewhat similar to a glass and at high temperatures it obeys Faraday's law. Haber[5] reported the electrolysis of an unglazed Royal Berlin crucible between electrodes of molten tin. This was carried on between temperatures of 330° to 1250°C and on analyzing the cathode tin he found sodium, potassium, aluminum, iron, calcium and magnesium to be deposited electrolytically. It was definitely shown that the relation between current strength and migration of metal ions held for hot porcelain, as it does for aqueous solutions. At the lower temperatures used, Haber believed the main silicate of porcelain, $Al_2(SiO_3)_3$, acts as solvent and the glassy silicates act as electrolytes. At about 1000°C the aluminum silicate also seemed to conduct. From this it would seem that only certain alkali silicates ionize at the temperatures of the experiments on solid glass (100–500°C), but that silicates of other metals dissociate at higher temperatures.

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[1] *Ann. Physik.*, **32**, 327 (1913).

[2] *Loc. cit.*

[3] Speranskii, *Jour. Russ. Phys. Chem. Soc.*, **47**, 52–58 (1915).

[4] *Compt. rend.*, **96**, 785–787 (1883).

[5] *Z. anorg. Chem.*, **57**, 154–173 (1908).

Silicates can be divided into two general classes, glassy and crystalline. Doelter[1] observed that glasses show no sharp bend at the melting point on conductivity-temperature curves, but that crystalline silicates show a marked change starting just below the melting point. When 200°C above or below the melting point, the conductivity of all the silicates studied was almost a linear function of the temperature. The temperature coefficient of solids was high, that of liquids was low. Doelter[2] concluded with many others, that the increase in conductivity with temperature is due mostly to increased mobility of the ions, and not to a great increase in ionization. Viscosity and elasticity may have some effect, especially the former, but there is no marked change in the conductivity of a glass at the melting point, where the viscosity is very great. Albite (sodium feldspar) formed one of the most viscous glasses, but it conducted best, and aluminum was found alloyed with the cathode.

The conductivity of many silicates was determined, using platinum electrodes in crucibles of a quartz-kaolin mixture. The results were too inaccurate, due to experimental difficulties, to give numerical data, but the general behavior was shown. Calcium metasilicate[3] ($CaSiO_3$) showed about the same conductivity with both the artificial product and the natural mineral (Wollastonite), giving no sharp change at the melting point. Calcium alumino-silicate [$2Ca\,SiO_3 . CaO . Al_2O_3$] shows a marked change at the melting point, indicating increased dissociation, and decreased viscosity.

Much work has been done on the electrical conductivity of molten salts,[4] and glass is but a mixture of salts. R. Lorenz and Kalmus,[5] used a capillary cell with good results. This cell consisted of two horizontal electrodes, separated by a capillary tube of glass or quartz. Such a cell could not be used for molten glass because of the difficulty of removing air bubbles from the viscous melt. U-tubes of porcelain were also employed

[1] *Monatsh.*, **28**, 1313–1380 (1908); **29**, 607–644 (1909).

[2] *Z. Elektrochem.*, **14**, 552–555 (1908).

[3] Doelter, *Zentr. Hydraul. Zemente*, **1**, 104–111 (1911).

[4] R. Lorenz, "Die Elektrolyse geschmolzener Salze." Wilhelm Knapp, Halle & S. (1908).

[5] *Z. physik. Chem.*, **59**, 17 (1907).

but these have the same objection as the capillary cells when used with molten glass.

Goodwin and Mailey[1] have determined the conductivity of molten lithium, sodium, potassium, and silver nitrates and silver chlorate, over long temperature ranges. The equivalent conductivity of mixtures of sodium and potassium nitrates was found to be about 3% less than that calculated by the law of mixtures. This indicates that these salts do not react and are probably highly ionized. If the deviation is not due to experimental error it would show less dissociation in mixtures with a common ion. In the case of silver chlorate and lithium nitrate, the conductivity was much below that calculated for the mixture. The equivalent conductivity of fused potassium nitrate, divided by the fluidity (reciprocal of viscosity), was found to be nearly a constant, gradually decreasing with increasing temperature. This behavior is common with most salts. From these facts, it would seem possible that sodium chloride in a soda-lime glass would give a lower conductivity than that calculated for the mixture, and this was found to be the case.

The following table gives a good comparison of the conductivity of fused salts with their conductivity in normal aqueous solutions.[2]

TABLE II

Salt	Temperature	Sp. condy., fused	N. sol. 18°C, sp. condy.	Equiv. condy. $t°$	Equiv. condy. 18°
$NaNO_3$	350°C	1.173	0.0660	52.87	105
KNO_3	350°	0.673	.0804	36.54	126
$AgNO_3$	350°	1.245	.0678	55.43	117
NaCl	850°	3.50	.0744	137.00	110
KCl	850°	2.30	.0982	117.00	131

Sandonnini[3] has also determined the electrical conductivity of molten salt mixtures. The values observed were always lower than those calculated for the mixtures, and the deviation was greatest for those pairs which formed compounds.

Experimental Work

Measuring Apparatus.—The electrical conductivity of the molten glass was measured by the improved method of Kohlrausch,[4] for electrolytes. A Vreeland oscillator operating on 110 volt d. c. was used giving an alternating current with a frequency of 1000. The arrangement of the apparatus is shown in Fig. 1. A known resistance and the re-

[1] *Phys. Rev.*, **25,** 469–489 (1908); **26,** 28–60 (1908).

[2] Goodwin, *Trans. Am. Electrochem. Soc.*, **21,** 105 (1912).

[3] *Atti. accad. Lincei*, **24** [1], 616–21 (1915); *Gazz. chim. ital.*, **501,** 289–321 (1920).

[4] Kohlrausch and Holborn, "Leitvermögen der Elektrolyte," Teubner, Leipzig (1898).

sistance of a conductivity cell were balanced in opposite arms of a Wheatstone bridge, the point of balance being determined by means of a sound minimum in a telephone receiver.

The bridge employed (Fig. 1-E) was of the usual drum-wound type, having ten turns of wire on a marble cylinder. The readings of the bridge wire could be estimated with great accuracy to one ten-thousandth of its total length. A 99,999 ohm resistance box (Fig. 1-B) with bifilar coils was used. Due to the large power factor of the larger coils of this type, resistance units higher than 100 ohms were not used. The resistance box was not calibrated, but it was checked by measuring the conductivity of aqueous solutions at room temperature. Checks could easily be made to 0.05% which is much below the error caused by other factors of the determination. A fairly sharp minimum in the telephones was maintained by balancing out the capacity of the cell by means of variable condensers (Fig. 1-A) connected in parallel across the resistance box. For this purpose a variable air condenser of about 0.0004 microfarad capacity, and two mica box condensers were employed. The latter had various convenient units from 0.001 to 0.5 microfarad with a total capacity of about 1.2 microfarads.

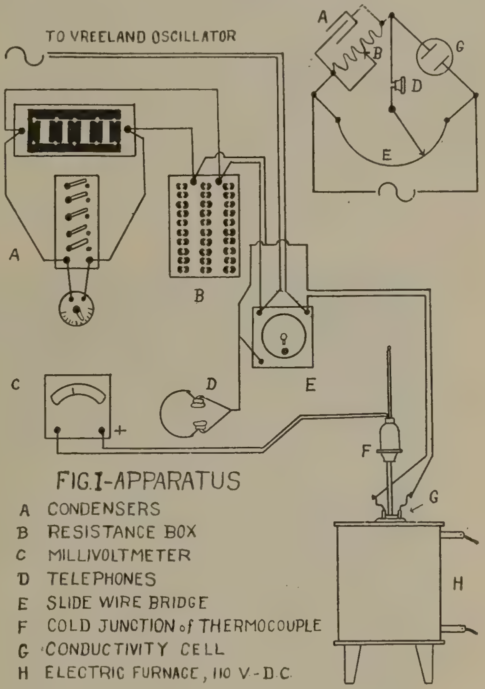

FIG. 1-APPARATUS

A CONDENSERS
B RESISTANCE BOX
C MILLIVOLTMETER
D TELEPHONES
E SLIDE WIRE BRIDGE
F COLD JUNCTION of THERMOCOUPLE
G CONDUCTIVITY CELL
H ELECTRIC FURNACE, 110 V-D.C.

Furnace.—The conductivity cell was heated in a 110 v. d. c. vertical furnace (Fig. 1-H) having a granular carbon resistance element. An ordinary nichrome wire-wound furnace would have been more suitable if it had not been necessary to raise the temperature much above 1000°C to free the glass from bubbles. By carefully adjusting the rheostat the temperature could be kept constant to less than a degree, for at least a minute. Ordinarily it took less than fifteen seconds to balance the bridge and get the temperature reading. At 1000°C the change in specific conductivity of the glass was about 0.6% per degree, while at 800° it was about 1.0%.

Temperature Measurements.—A platinum—(90% platinum, 10% rhodium) thermocouple was used in all temperature measurements of the glass. The cold junction (Fig. 1-F) was kept in an iron jacket at the end of the porcelain protection tube, and its temperature was measured by a 200° thermometer inserted between the leads. The millivolt reading was taken on a Weston, model 322, pyro-millivoltmeter (Fig. 1-C).

The thermocouple was calibrated under working conditions by the melting points of pure electrolytic copper covered with graphite (1083°), of sodium chloride (801°), and of pure zinc covered with graphite (419.4°). The furnace was heated about 50–100° above the melting point of the substance and then the thermocouple was carefully inserted to about two-thirds the depth of the melt.

For practical reasons the thermocouple was calibrated with a cold junction temperature of 30°C, and under working conditions the extreme deviation was ±10°. For this type of couple the correction to be added to the temperature calculated from the millivolt reading is small.

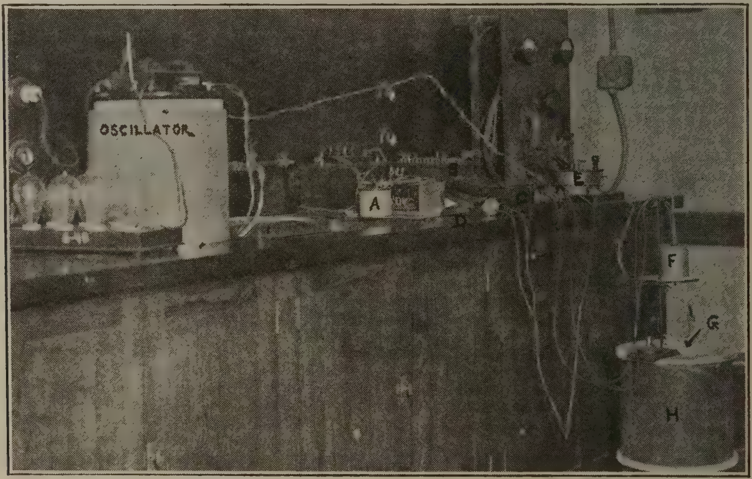

Fig. 1-*a*.

The calibration was carried out according to directions given by the U. S. Bureau of Standards.[1]

Conductivity Cell.—(Fig. 1-G and Fig. 2.) By far the greatest difficulty in this work was to obtain a cell that would meet the necessary requirements. Briefly, these are as follows:

1. The material must be as nearly a non-conductor as possible at the high temperatures to which it is subjected.

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[1] "Pyrometric Practice," Bur. Stand., *Tech. Paper* **170,** 54–55, 189–206, 234–239 (1921).

2. It must not shrink or soften at the temperature used, and must not contaminate the molten glass to any great extent.
3. The coefficient of expansion should be as small as possible to keep the temperature coefficient of the cell constant quite low.
4. The material must be plastic in its preparatory stage, to be molded into suitable shape and to hold the electrodes firmly.
5. The electrode metal should conduct well, should be chemically inert towards glass, have a high melting point, and if possible, low coefficients of expansion and resistance.

Several attempts were made to produce cells before a suitable type was obtained. The first attempt consisted of a special furnace cover molded of fire clay to hold two quartz insulating tubes, which converged in the center of a porcelain crucible set in the furnace chamber. Sheet platinum electrodes about 1 cm. square and 1 cm. apart were employed. The size and distance apart of the electrodes could easily be adjusted and a cell constant could be determined, but there was danger of bending the electrodes when placing apparatus in the furnace. It was also practically impossible to replace the electrodes in exactly the same position in the crucible after getting their resistance capacity. This could be avoided in a much larger crucible containing a large batch of glass, where the walls would not interfere with the "edge effect" of the conductivity between the electrodes. Larger crucibles, however, cannot be employed in the furnaces suitable for this work, due to lack of uniformity of temperature. The greatest objection was that the electrodes were not rigid enough to allow the bubbles to be removed by stirring.

The second attempt was similar to the first except that heavy nickel rods were used for electrodes, extending through heavy quartz insulating tubes. Here the electrodes were rigid and bubbles could be removed, but the "edge effect" would cause error if the same setting in the crucible were not reproduced after determining the cell constant. A series of experiments showed that it was not possible to reproduce exactly the electrode position and that considerable error might arise.

The third cell was like the second in principle, but more elaborate. A porcelain form was made which held the nickel rods and also served as container for the glass. Here the bubbles could be removed less readily than in the second type, but the electrodes were always in the same relative position. In both this and the preceding cell, however, there was considerable expansion of the nickel rods on heating. Nickel is a suitable electrode material if protected from oxidation, or if the bright metal is suddenly immersed in the molten glass. The rods could not be held tightly, due to their great expansion, and corrections could not easily be determined. The cell was abandoned after several determinations failed to give check results.

The final form of cell adopted for this work is shown in Fig. 2. Porcelain and platinum were chosen as the most suitable materials.

The porcelain was made from the best commercial grade of materials obtainable on the market. The quartz and feldspar were already finely ground, and by further grinding in a mortar and subsequent mixing with water, the clays could easily be brought to a fine state of division. The powdered materials were weighed, mixed dry, and then thoroughly mixed with water until a uniform plastic body was obtained. The composition was as follows:—

Ground quartz	34 parts by weight
Potash feldspar	16 parts by weight
Tennessee ball clay No. 3	20 parts by weight
North Carolina kaolin	40 parts by weight

The platinum electrodes were made from platinum foil 0.05 mm. thick, cut into pieces one centimeter square or slightly larger. A 2.5 cm. length of No. 24 B. & S. gage platinum wire was welded to each of two diagonally opposite corners, which were then bent at right angles to the foil. The other two corners were also bent about 3 mm. in the same direction, so that when the electrode was embedded in the plastic porcelain body, it was firmly held in place (Fig. 2-A), and could not be bent after the porcelain had been fired. The two wires were passed through the cell walls (Fig. 2-B) and connected to the leads of the cell when in use.

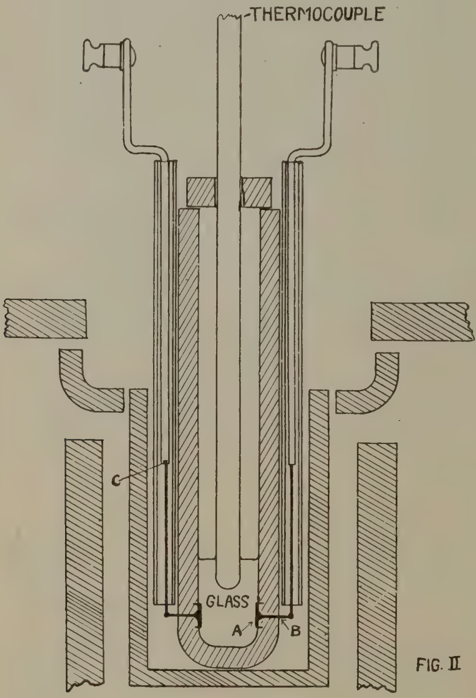

FIG. II

The cell itself was made by molding the wet porcelain mixture around an eight-inch test tube. The wall thickness was approximately 5 mm. and great care had to be taken to knead the mixture and roll it until the thickness was uniform and all laps were thoroughly joined. A hole was filed into the end of the test-tube, so that by twisting the tube around and slowly withdrawing it, it could be removed without causing the cell walls to collapse, or otherwise deform.

The electrodes were inserted while the soft body was still around the glass tube. To do this the cell was cut about 4 cm. from the closed end. The end piece was removed by a twisting motion and set on a glass plate, and the electrodes were then inserted on the inside about 1 cm. from the end. After pushing into place and pressing the porcelain closely around the corners, the end piece was again placed over the tube and the two parts worked together. Great care had to be exercised in joining these parts. If they were not well kneaded and twisted back and forth at the union, the cell would very often crack at this point on burning.

When completely molded, the cell was laid on its side on a plaster of Paris slab and the test-tube was withdrawn. After thorough drying, the cell was carefully examined to make sure no porcelain mixture was on the platinum electrodes. The cell was then burned in a gas-fired "Surface Combustion" furnace. The temperature was raised slowly to about 1400°C where it was held for about three hours. This was to make the porcelain dense and free from pores and to insure against further shrinkage when the cell was in use. The average time of burning was about nine hours.

The leads into the furnace were made as heavy as possible to have a very low resistance and temperature correction. Soft iron wire 0.312 cm. in diameter and 15 cm. long was used from the binding posts to the high temperature zone. Two 7.5 cm. lengths of No. 20 B. & S. gage platinum wire were twisted together and connected to the iron wire by drilling into its end, inserting the platinum (Fig. 2-C) and squeezing in a vice. The lower end of the platinum was connected to the wires of the cell by twisting and welding. The leads in the furnace were protected by porcelain insulating tubes, and the whole apparatus was sealed into the chamber of the electric furnace which served as an air bath tightly closed by means of a plastic fire clay and quartz sand mixture.

Preliminary Work

Soda-Lime Glass.—The glass used in this work was made from analyzed sodium and calcium carbonates and a high grade quartz sand. The raw batch was well mixed and melted in covered $4^1/_2$ inch Denver Fire Clay crucibles. The melts were made in a "Surface Combustion" furnace in about eight hours, the final temperature being about 1400°C. The molten glass was poured into iron button molds to cool. It was clear with a light bluish green tint in thick sections.

Analysis.—In order to obtain uniform samples, the glass was ground in a steel mortar, passed over a magnet, through a 100-mesh sieve, then thoroughly mixed and analyzed by standard methods.

The results of the analysis follow:

	Average
SiO_2	67.37%
CaO	16.74
Al_2O_3	.41
Fe_2O_3	.09
Na_2O	15.60
	100.21

Conductivity studies discussed later include solutions of salt in glass. The amount of sodium chloride added to the glass was determined by weighing the chlorine as silver chloride. This analysis was similar to that of the glass itself.

Specific conductivity values employed for potassium chloride solution were those obtained by Kohlrausch.[1]

Procedure

When the cell constant had been obtained, the cell was set in the furnace and sealed in place by plastic fire clay. The thermocouple was inserted and the temperature raised to 1200° in about three hours. The resistance of the empty cell was determined at 100° intervals to make a correction which generally was about +0.6% of the apparent resistance of the glass at 1000°. The resistance of cell No. 12 is given here as a typical example:

Temperature	Resistance	Temperature	Resistance
777°	11,600 ohms	1113°	1,600 ohms
855	6,500	1196	1,190
944	3,720	1228	1,110
1040	2,220	....	.....

While heating, the cell was closed with a porcelain stopper and the thermocouple. These were then removed and 25 grams of the powdered glass introduced. The temperature was raised to 1400°, until the glass was completely melted and most of the air bubbles were removed. The bubbles would stick to the platinum electrodes and were the greatest source of error. Stirring with a bright nickel or platinum rod while the glass was at high temperatures, was the only effective means of removing bubbles. The glass was freed from bubbles in as short a time as possible and the temperature lowered to about 1100° when the thermocouple was again inserted. It was necessary to determine the proper position of the thermocouple in the glass by experiment. If inserted too deeply it interfered with the conductivity measurements causing error. If not deeply enough there was a temperature error, as the glass had a temperature variation of 10–20° between its center and the upper surface. By adjusting the furnace rheostat and an auxiliary rheostat and letting the current flow constantly for 30–60 minutes, the temperature became constant around 1050°. The thermocouple was then lowered from its normal position until it was between the electrodes, and the millivoltmeter was read to learn if there was a difference of temperature. As a rule, the glass was several degrees hotter between the electrodes than around the thermocouple about 1 cm. above this point. A proportionate correction was made, and this correction decreased regularly as the furnace temperature approached room temperature.

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[1] Kohlrausch, Holborn and Dieselhorst, *Ann. Physik.*, **64,** 417–410 (1898); "Physikalisch-Chemische Tablellen," Landolt-Börnstein, Springer, Berlin, 1117 (1912).

When the temperature became constant, the oscillator was started and the resistance of the box was adjusted until the setting of the slide-wire was as near its center as possible. The variable condensers were then adjusted until the sound minimum was sharp and did not extend over more than two scale divisions. The bridge was balanced, and the millivoltmeter immediately read, after tapping the instrument to insure correct needle position. Several readings were made at a given temperature. The rheostat resistance was then increased and the current was turned off for 2–5 minutes and then turned on again for at least half an hour before the readings were taken. In this manner the temperature was lowered and held constant for conductivity measurements in approximately 50° steps. Readings of the known resistance, millivoltmeter, cold junction temperature, capacity and bridge setting were recorded. The time was also recorded to obtain the rate of cooling. Specific conductivity measurements were made from 750–1050°. The resistance of the glass changes so much over this range (about 0.7% per degree) that higher temperature measurements would call for a cell of greater resistance. The lower temperature (750°) is in the solidification range of the glass.

The cell constant is influenced slightly by temperature. It is increased when the distance between the electrodes is increased, and decreased by increasing their area. The average temperature coefficient of linear expansion of the porcelain between 0–1000° is about 0.000005. The average coefficient for platinum over the same temperature range is approximately 0.00001. On this basis, the cell constant increases by about 0.2% from room temperature to 1000°. The iron and platinum lead-in wires of the furnace increased in resistance as the temperature rose. The corrections for the cell constant and that for resistance of the leads were of opposite sign to, and almost equivalent to the correction for the conductivity of the porcelain in the cell, so practically no corrections were necessary between 750° and 1050°C.

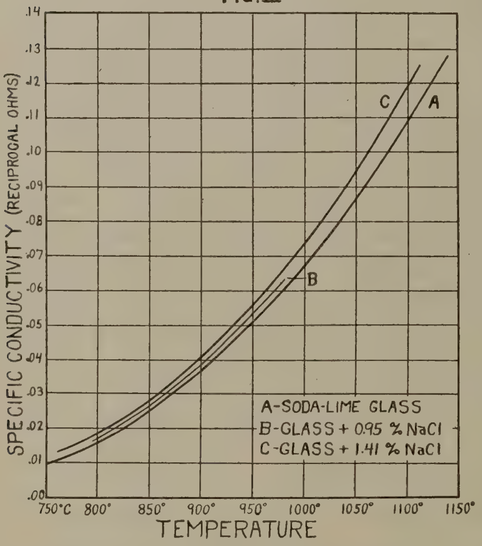
Sodium chloride was added in 0.2, 0.4, 0.6, 0.8 and 1.0 g. lots, respectively, per 25 g. portion of glass. Baker and Adamson Chemical Company's C. P. product re-tested was employed. It was mixed with the powdered glass just before introduction into the cell. The sodium chloride vaporized partially at these high temperatures and so the amount found in the glass was always smaller than the amount of salt originally introduced. In the case of the two higher concentrations some salt was found on the surface of the glass after cooling, due to limited solubility. The highest portion of salt found in any specimen of glass in this investigation was 1.41%. Gelstharp[1] studied plate glasses containing sodium chloride and sodium sulfate. These were added as raw materials and in the glasses examined the sodium chloride content varied from 0.91% to 1.48%. By increasing the time or temperature of melting the sodium sulfate and chloride content was found to decrease. No change in properties due to the presence of the salts was noticed by Gelstharp, and there was no apparent difference in appearance of the glass used in this research, except a possible tendency toward devitrification. This was noticed in two specimens and occurred around the bottom of the thermocouple.

After a determination the cells were broken open and the glass examined. In every case the glass was of a light yellow-green color and nearly free from bubbles. Many cells had bubbles on the electrodes and so these determinations were discarded.

Discussion of Results

Accuracy in conductivity measurements in aqueous solutions, through introduction of improved apparatus, is of a high order. Work at the high temperatures encountered in this research is naturally less accurate for lack of control over the conditions. The results of the determinations are best shown in Fig. 3. Curve A represents the mean of four determinations of the conductivity of glass itself. Curve B shows the determination when the glass contained 0.95% NaCl and curve C when it contained 1.41% NaCl. Determinations were also made when the glass contained 1.08% and 1.30% of salt. These displayed more discrepancies than the others and are not shown in the curves. The main cause of these deviations was the variation of current in the furnace with consequent failure to keep the temperature constant.

FIG. III



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[1] *Trans. Amer. Ceram. Soc.*, **14**, 655–70 (1912).

The following table gives conductivity values at various temperatures. Above 1050° the resistance of the glass in the cells became so low that sometimes capacities as high as 3 or 4 microfarads would have been necessary to produce a sharp sound minimum. This condition makes the data taken above that temperature less reliable. It is interesting to note that conductivity increases with temperature in vitreous silicate media as in aqueous solutions.

TABLE III

SPECIFIC CONDUCTIVITY

Temperature, degrees	Soda-lime glass	Per cent NaCl per 100% glass		
		0.66%	0.95%	1.41%
750	0.0099	....	....	....
800	.0163	0.0168	....	0.0184
850	.0254	.0262	0.0267	.0278
900	.0368	.0379	.0387	.0404
950	.0510	.0525	.0532	.0553
1000	.0680	....	....	.0732
1050	.0877	....	....	.0947
1100	.1097	....	....	....

The greatest deviations from the mean determination for the glass itself were about ±2.5%, but most of the values were within ±1.0%.

In Table II the specific conductivity of molten sodium chloride at 850° is 3.50. Adding 1.41% of sodium chloride to 100 of glass increases the conductivity at this temperature by about 9.41%. The conductivity at this temperature was calculated from the percentage composition as 0.0751, while the measured value was only 0.0278 and the conductivity of the pure glass was 0.0254. The calculated value of the conductivity of molten salts is also more than the observed value, the deviation being small for pairs of salts such as sodium and potassium nitrates which are highly ionized and do not react.[1] When the salts form compounds the deviation is much greater.[2] In any case the amount of sodium chloride introduced into a glass is small and experimental error makes the drawing of absolute conclusions somewhat risky.

It has been shown that in solid glass only the alkali metals are ionized at temperatures around 200–400° and about 80% of the sodium in a soda-lime glass is in the ionic state. It has also been suggested from the behavior of other complex silicates that at higher temperatures (600–1200°) silicates such as calcium and aluminum are ionized. This may partially account for the increased conductivity of glasses at very high temperatures. The viscosity is considerably lowered on melting, but the change in conductivity of the glass at temperatures in the softening range is much less than that of the viscosity itself, so other factors must be considered. The conductivity of a soda-lime glass at 100°C[1] is near the order of magnitude of 10^{-10} while at 750° for the glass in this work it is 9.9×10^{-3}. By approximate extrapolation of the curve in Fig. 3 the conductivity-temperature relation from room temperature to 1200° can be shown. It is possible when the glass is fluid that the silicate ions can also transport electricity as well as the mobile sodium ions.

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[1] *Phys. Rev., loc. cit.*

[2] *Atti. Accad. Lincei, loc. cit.*

In the past it has been customary to furnish data or discuss the conductivity of "soda-lime glass," and some investigators do not even give the latter information, simply using the term "glass" and omitting the analysis. It has been shown that the sodium content of a glass can have an important effect on its conductivity. Data to show the effect of other constituents such as CaO, Al_2O_3, etc. are meager. It is apparent that the composition of glass is so varied that classification of conductivity in general terms is undesirable.

Conclusions.—This investigation embraces a review of past work, a study of apparatus and methods for determining the conductivity of glasses and solutions of salts in vitreous media above the melting point of the solvent. Pioneer work in this field is time-consuming to a large degree before the actual determinations can be made. Hence, while conductivity data furnished are limited, the way has been paved for future work and the following conclusions and possibilities are likely.

1. A search of the literature indicates that this work is the first study of the electrical conductivity of salts dissolved in molten silicates. The conductivity of mixtures of sodium chloride and molten glass is similar in nature to other molten salt mixtures.

2. The conductivity of a soda-lime glass increases in proportion to the amount of sodium chloride added. The increase is sufficient to show ionization although the conductivity of the salt is not nearly as great as it is in molten sodium chloride at a given temperature. This might be due to several changes, such as the viscosity change in the glass, common ion effects, reaction to form compounds, etc.

3. The maximum value of sodium chloride found in plate glass by Gelstharp was 1.48%. It has been checked in this work by a value of 1.41%, though in the glasses studied by Gelstharp the salt was added to the raw batch while in this work it was added to the finished glass.

4. This investigation indicates that apparatus used for making electrical conductivity measurements of aqueous solutions is suitable for work with molten glasses when the cell described is used with suitable lead-in wires and furnace. Jaeger and Kapma[2] have described a method which has good precision, where two platinum crucibles, one inside the other, act both as container and electrodes. The resistance of such an

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[1] Campbell, *Proc. Phys. Soc.* (London), **25**, 336 (1913)

[2] *Z. anorg. allgem. Chem.*, **113**, 27–58 (1920).

arrangement cannot be made very high and would require large capacities. In a glass at very high temperatures, considerable alkali might be lost by volatilization. This might not make much difference with a pure salt, but in glass where the sodium content very largely determines the conductivity, it would be important.

5. The electrical conductivity of the glass is small from 0° to 750°C, compared with the conductivity at higher temperatures. It is possible to extrapolate approximately curve A in Fig. 3 and to study the conductivity of this glass from 0–1200°C. The expression $C = a + bt + ct^2$ has been applied to the conductivity-temperature relation, where C = specific conductivity, a, b, and c are constants and t is the temperature. The constants were calculated from experimental data. The equation will fit the curve above the melting point (800–1100°) fairly well and other investigators have applied it to solid glass (100–500°), but an attempt to fit the entire extrapolated curve (0–1200°) failed. Most probably there is discontinuity at the melting point of the glass where all factors have not yet been accounted for.

6. Since sodium ions are present in opal glasses without destroying opalescence, and since the addition of negatively charged chloride or sulfate ions will remove this effect, the colloid present must be positive in its nature, if the opalescence is due to colloidal material as generally assumed. This seems to resemble the coagulation of colloidal particles in aqueous solutions by the addition of ions of opposite charge. If the colloid in molten glass is Al_2O_3, then it is probably positive as colloidal $Al_2O_3 . xH_2O$ is positive in aqueous media. Since many positive sodium ions are present in opal glass the coagulation by added salt must be due to negative chloride ions.

7. Conductivity and electrolytic investigations of molten glasses of various types will most probably do much to show the nature of vitreous silicate solutions and permit of comparison with aqueous solutions. Similarity has already been implied.[1] To obtain reliable and far-reaching results, a combination study of viscosity, density, conductivity and ionic mobilities would be necessary.

8. A molten glass is most probably in equilibrium and the equilibrium in the solid state, which has been more carefully studied than in molten material, is undoubtedly different in degree, rather than in nature. This has been shown by the tempering of a glass on cooling, when the conductivity is more nearly that of the molten glass, than it is in a glass which has been slowly annealed. Research on such equilibria will probably lead to an understanding of reactions at high temperatures and of the structure of complex silicates.

[1] A. Silverman, *Jour. Ind. Eng. Chem.*, 9, 33 (1917).

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EXACT NOTIONS OF FLUORINE ENAMELS

By Charles Musiol[1]

ABSTRACT

The theories of Vogt, Grunwald, Mayer and Havas, and others regarding the rôle of fluorine in enamels are proved by mathematical rather than chemical means to be incorrect. Fluorine is not volatilized as SiF_4, but disappears during the smelting process as F_2, although in the presence of B_2O_3 it may be volatilized as BF_3. Enamel formulas should be studied by means of the "*subtractive*" analysis method.

Introduction

Enamels used in sheet iron and cast iron enamel works are nearly all fluorine enamels. Their compositions vary according to the qualities the enamel must possess, namely, fusibility, fluidity, coefficient of expansion, opacity, and other physical and chemical qualities.

Generally fluorine enamels are solid solutions of different silicates, with which is blended the fluorine issuing from fluorine compounds, such as fluorides of aluminium, barium, calcium, sodium, natural cryolith, artificial cryolith, sodium silico-fluoride, chiolith, and others.

The effect produced by the use of simple compounds, such as Na_2O, K_2O. . . . SiO_2, etc., either basic or acid, has been defined in a more or less exact way in numerous studies of glasses and glazes. We cannot, however, say as much in regard to the effect of fluorine and fluorine compounds. Sometimes it is entirely neglected, and even omitted from formulas, as in J. B. Shaw's paper on "The Admissible Limits of the Ingredients of Sheet Iron Enamels."[2]

Fluorine Glazes and Enamels

At the Seventh International Congress of Inorganic Chemistry in London in 1909, G. Vogt, director of the National Manufactory of Sèvres, presented a very complete study of *a porcelain glaze containing fluorine,* so as to determine what part fluorine takes in fluorine glazes. This glaze had been prepared according to the molecular formula:

$$\left.\begin{array}{l} 0.70\ \text{CaO} \\ 0.30\ \text{Na}_2\text{O} \end{array}\right\} 0.50\ \text{Al}_2\text{O}_3 \left\{ 4.0\ \text{SiO}_2 \right.$$

and was smelted at 1300°C. The batch mixture as well as the fritted glaze were analyzed, with results as shown in Table I.

The comparison of these two analyses led Mr. Vogt to the following conclusions: "These results prove that all the fluorine, introduced into the glaze by fluorspar, has disappeared during the smelting, according to the reaction:

$$SiO_2 + 2CaF_2 = SiF_4 + 2CaO$$

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[1] Formerly Enamelworks director, now Technical Bureau at Brussels.

[2] *Trans. Amer. Ceram. Soc.*, **11**, 103 (1909); *Jour. Amer. Ceram. Soc.*, **3**, 492 (1920).

That this reaction really took place is proved by the resemblance of the molecular formula of the fritted glaze,

$$\left.\begin{array}{l}0.715\ CaO\\0.285\ Na_2O\end{array}\right\}0.52\ Al_2O_3\left\{4.4\ SiO_2\right.$$

to the molecular formula, mentioned above, which served as a basis for the preparation of the glaze. The result obtained indicates that a mixture for a fluorine glaze to be smelted under the same conditions and at a temperature of 1300°C ought to contain a certain excess of SiO_2, the quantity whereof would be equivalent to the one which disappears in the form of SiF_4, so that the percentage of SiO_2 should not decrease during the fritting." As it happens, Vogt's name was so renowned in the ceramic world that nobody dreamed of doubting the accuracy of his hypothesis.

TABLE I

	Raw batch, per cent	Fritted glaze, per cent
SiO_2	68.22	70.84
Al_2O_3	13.89	14.12
CaO	3.06	10.41
Ca	4.91	....
F_2	4.65	....
$Na_2O + K_2O$	5.27	4.63
	100.00	100.00

Bock is authority for the statement:[1] "Soon after the melting of the enamel, the fluorine combines with the silica and vanishes under the form of silicon tetrafluoride."

Without submitting confirming data, Grunwald[2] affirms that during the melting of an enamel containing fluorspar, a part of the fluorine disappears in the form of silicon fluoride (SiF_4) according to the reaction

$$2CaF_2 + 3SiO_2 = 2CaSiO_3 + SiF_4.$$

He also maintains that the melting of an enamel containing cryolith is accompanied by the partial disappearance of silicon tetrafluoride.

Expressing more or less the same opinions, Eyer[3] came to the conclusion that the silicate of calcium thus formed melts with difficulty and renders enamels fragile.

In an article entitled "Phenomena of the Melting of Enamels,"[4] Mayer and Havas have published the results of their experiments with fluorine enamels. Below are two analyses of one of these enamels—one an "ideal" analysis of the batch mixture calculated from the analysis of the materials used, and the other an actual analysis of the melted mixture:

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[1] *Sprechsaal*, **40** (1908).

[2] "Abhandlungen aus der Emailtechnik," pp. 146, 153, 154 (1910); "Chemische Technologie der Emailschmaterialien," pp. 30, 109 (1911); "The Raw Materials for the Enamel Industry," pp. 22, 84 (1914).

[3] Emailwissenschaft, **1913**, page 50.

[4] *Sprechsaal*, **1** (1911).

TABLE II

	"Ideal" analysis raw batch, per cent	Actual analysis melted batch, per cent
SiO_2	50.48	51.00
B_2O_3	16.34	15.79
CaF_2	6.81	5.44
CoO	0.27	0.25
MnO	0.67	0.71
Al_2O_3	7.75	7.86
CaO	0.23	1.51
K_2O	2.38	2.60
Na_2O	15.07	14.84
	100.00	100.00

From a comparison of the mixture analysis and of the melted ground coat analysis, the experimenters drew the following conclusions:

> It is evident that 20.2% of the amount of fluorine, and 3.4% of the amount of boric acid which were originally present disappear. The small increase of silica (SiO_2) is surprising, but may be explained by the fact that the fluorine escapes in the form of silicon tetrafluoride (SiF_4). The loss of boric acid is due to its great volatility at the melting temperature of 1000–1100°C. However, the fact is also recognized that a portion of the fluorine, combining with the boron, escapes in the form of boron fluoride (BF_3).

E. P. Poste and B. A. Rice[1] who, however, purposely refrained from introducing analyses of the enamels tested by them, found that the fluorine of their enamel was completely volatilized as silicon tetrafluoride (SiF_4). In the absence of their complete data, their results cannot be discussed.

Other references[2] might also be cited, but they only repeat what has already been said.

But let us consider the conclusions which these investigators have drawn:

If Grunwald and Eyer had studied the tests of the Russian Karandeef, and of the American experimenters Day, Allen, Shepherd, White, and Wright, they would have learned that the melting point of the lime silicate $CaO.SiO_2$ is in the range 1500–1550°C, and they would have deducted that at the quite lower temperature at which enamels are melted, the forming of calcium silicate is *impossible*.

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[1] *Jour. Amer. Ceram. Soc.*, **1**, 221 (1918).

[2] "Ceramic Chemistry, de Stephenson," p. 46 (1912); U. S. Bur. of Standards, *Tech. Paper* **165**, pp. 28, 54.

If the fluorine had disappeared according to the reaction suggested by Vogt,

$$SiO_2 + 2CaF_2 = SiF_4 + 2CaO$$

then the volatilization of each F_4 to be found in the SiF_4 would cause the loss of one SiO_2, or, considered from a molecular weight standpoint, the loss of one part by weight of F_2 must cause a loss of 0.795 parts by weight of SiO_2. Since the analyses as given in Table I indicate a loss of 4.65% of fluorine, the silica ought to have undergone a loss of 3.695%. At the same time each Ca of the CaF_2 ought to have reappeared as CaO, which is 1.397 times heavier, or 4.91% of Ca in the raw batch should give 6.86% of CaO in the fritted glaze. Hence, according to Vogt's suppositions, the analysis of the fritted glaze ought to be as follows:

TABLE III

	Analysis raw batch, per cent		Theoretical analysis according to Vogt's suppositions, per cent	Actual analysis of Vogt's fritted glaze (see Table I), per cent
SiO_2	68.22 — 3.695	= 64.525	68.900	70.84
Al_2O_3	13.89	= 13.890	14.835	14.12
CaO	3.06 + 6.86	= 9.920	10.600	10.41
Ca	4.91 — 4.91	= 0.000	....	....
F_2	4.65 — 4.65	= 0.000	....	....
Alkalies	5.27	= 5.270	5.630	4.63
	100.00	93.605	99.965	100.00

Since Vogt's analysis contains more SiO_2 and less alkalies than would be present had the process taken place according to the reaction he suggests, it would seem that his theory may be at fault.

However, in studying the situation which has caused this misapprehension, we see that Vogt has set up for comparison two analyses, which, according to a mathematical standpoint, are really not comparable, for an analysis containing Ca + F_2 cannot be compared to an analysis where the same Ca is expressed as CaO. Vogt has also neglected the fundamental rule of Lavoisier, whose celebrated saying, *Nothing is lost,—nothing creates itself*, is well known. One cannot compare CaF_2, which has a molecular weight of 78, with the expression CaO + F_2, which has a molecular weight sum of 94.

It is evident that to completely satisfy *Lavoisier's rule*, the expression should be

$$CaF_2 = CaO + F_2 - O$$
$$78 = 56 + 38 - 16.$$

This relation teaches us that in the analysis of fluorine enamels, *it is necessary to deduct 16 ÷ 38 = 0.421 parts by weight of oxygen from each part by weight of fluorine contained in the enamel.*

"Subtractive" Method of Analysis

To thoroughly distinguish this new method of calculation from the old one, we will call it a "*subtractive*" one. In Table IV, below, the method of transforming Vogt's raw batch formula into the "*subtractive*" analysis is shown:

TABLE IV

	A	B	C	D	E	G
SiO_2	68.22	....	68.220	68.220	70.125	70.680
Al_2O_3	13.89	....	13.890	13.890	14.270	14.390
CaO	3.06	6.86	9.920	9.920	10.200	10.278
CaF_2	9.56	....	.....	....	.....	....
F_2	....	4.65	4.650	....	.....	....
Alkalies	5.27	....	5.270	5.270	5.415	4.630
	100.00	11.51	101.950	97.300	100.010	99.978
−O	....	1.957	1.957	....	.....	....
	100.00	9.553	99.993	97.300	100.010	99.978

A = analysis of Vogt's Raw Batch—see Table I.
B = CaO and F_2 represented by 9.56% CaF_2.
C = total of columns A + B.
D = same as C minus the fluorine.
E = column D divided by factor 0.973 to bring analysis total to 100.
G = same analysis corrected by fact that part of alkalies volatilized and only 4.63% is shown by analysis, and assuming that no other substances than fluorine and the alkalies suffer fire loss.

Table V, below, shows a comparison of Vogt's analysis of the fritted glaze and the "*subtractive*" analysis:

TABLE V

(Showing how closely two analyses agree)

	Vogt's analysis, per cent	Subtractive analysis, per cent
SiO_2	70.84	70.68
Al_2O_3	14.12	14.390
CaO	10.41	10.278
Alkalies	4.63	4.630
	100.00	99.978

From the above it may be concluded that the fluorine has disappeared either alone, and that the alkalies and alumina have suffered their loss independently, or that the fluorine has vanished in the form of Na_2F_2, K_2F_2, and Al_2F_6. Whatever may be the case, it is shown that there is no loss of silica (SiO_2) and that consequently there is no forming of silicon tetrafluoride (SiF_4), as Vogt supposed.

If we take Mayer & Havas's results in their original form (see Table II), rearranging the order of constituents for convenience sake, and transform them into a "*subtractive*" analysis, we shall be better able to discuss them. If we suppose, with these authors, that only the fluorine (F_2) and boric acid (B_2O_3) suffer fire loss, using the same methods of calculation employed before, we obtain the "*subtractive*" *analysis* given in column "C s" below:

TABLE VI

	A	B	C	D	E	G	C s
Na_2O..........	15.07	....	15.070	14.84	....	14.840	15.240
K_2O...........	2.38	....	2.380	2.60	....	2.600	2.407
CaO...........	0.23	4.8896	5.120	1.51	3.906	5.415	5.178
CoO...........	0.27	....	0.270	0.25	....	0.250	0.273
MnO...........	0.67	....	0.670	0.71	....	0.710	0.678
RO............			23.510			23.815	23.776
B_2O_3..........	16.34	....	16.340	15.79	....	15.790	15.790
Al_2O_3..........	7.75	....	7.750	7.86	....	7.860	7.837
SiO_2...........	50.48	....	50.480	51.00	....	51.000	51.048
CaF_2...........	6.81	....	.....	5.44	....	.....	.....
F_2.............	....	3.3165	3.316	....	2.6493	2.649	2.649
	100.00	8.2061	101.396	100.00	6.5553	101.114	101.100
−O............	....	1.3965	1.396	....	1.115	1.115	1.115
	100.00	6.8096	100.000	100.00	5.4403	99.999	99.985

A = Ideal analysis of raw batch (see Table II).
B = CaO and F_2 to be derived from 6.81% CaF_2.
C = "*Subtractive*" *analysis* derived from A.
D = Actual analysis of melted batch (see Table II).
E = CaO and F_2 equivalent to 5.44% CaF_2.
G = "*Subtractive*" *analysis* derived from D.
C s = Ideal "*Subtractive*" *analysis*, calculated from "C," and assuming $B_2O_3 =$ 15.790; F_2 = 2.649; and O = 1.115.

The subtractive analysis "C s" can be calculated much more rapidly in a direct way by multiplying each constituent of the analysis "C" by a coefficient "s," derived as below:

$$S = \frac{100 - F + O}{100 - f + o} \times \frac{100 - B}{(100 - b) \times \dfrac{100 - F + O}{100 - f + o}}$$

where B = wt. of boric acid in analysis G
F = wt. of fluorine in analysis G
O = wt. of oxygen in analysis G

b = wt. of boric acid in analysis C
f = wt. of fluorine in analysis C
o = wt. of oxygen in analysis C

$$\text{Then}\quad S = \frac{100 - 2.649 + 1.115}{100 - 3.316 + 1.396} \times \frac{100 - 15.79}{(100 - 16.34) \times \dfrac{100 - 2.649 + 1.115}{100 - 3.316 + 1.396}}$$

$$= 1.00393 \times \frac{84.21}{83.66 \times 1.00393}$$

$$= 1.00393 \times \frac{84.21}{83.596} = 1.01126$$

In Table VII (below), by multiplying the different constituents of column "C" (Table VI), (fluorine, boric acid, and oxygen excepted) by the coefficient "s" = 1.01126 and borrowing from the analysis "G" that

B_2O_3 = 15.790
F_2 = 2.649
and O_2 = 1.115

we obtain the Ideal "Subtractive" analysis "C s" given above.

TABLE VII

	C	Coefficient s	C s
Na_2O	15.070	1.01126	15.240
K_2O	2.380	1.01126	2.407
CaO	5.120	1.01126	5.178
CoO	0.270	1.01126	0.273
MnO	0.670	1.01126	0.678
RO	23.510	.....	23.776
B_2O_3	16.340	.....	15.790
Al_2O_3	7.750	1.01126	7.837
SiO_2	50.480	1.01126	51.048
F_2	3.316	.....	2.649
	101.396	.....	101.100
−O	1.396	.....	1.115
	100.000	.....	99.985

From a comparison of the two subtractive analyses (columns G and C s in Table VI) we see

(1) That the silica (SiO_2) and alumina (Al_2O_3) have not suffered any change exceeding the limits of analytical mistake,

(2) That the sum of the alkalies ($Na_2O + K_2O$) has changed but little, but that the phenomena of the decrease of Na_2O and the simultaneous increase of K_2O are unexplainable,

(3) That the CaO has increased somewhat through an unknown cause,

(4) That, however, the amount of the bases RO has remained without any change of note.

Fluorine undergoes only a partial volatilization and there is a small loss of boric acid (B_2O_3).

As there is no decrease of silica (SiO_2) *there cannot be any formation of silicon tetrafluoride* (SiF_4) *whatever.*

However, we must call attention to the discrepancies in the analysis. Why the great increase in CaO, the decrease of Na_2O and of CoO, and the increase of K_2O and MnO? Are these caused by the inaccuracy of the analysis or by an error of writing?

Space allowed in this *Journal* will not permit a detailed study of the other ground coats,[1] but suffice it to say that in all these studies the constituents Na_2O, K_2O, and CaO behave quite erratically, sometimes increasing and sometimes decreasing, but that the silica (SiO_2) either does not change, or at worst, loses but a fraction of a per cent, and not enough to cause the loss of an appreciable amount of fluorine as silicon tetrafluoride (SiF_4).

Analyses are submitted by Mayer and Havas in which the enamel under consideration was smelted at higher temperatures than formerly, and in these cases the loss of fluorine increases. However, it is probably because of the higher smelting temperature that the volatilization of fluorine increased.

Fluorine Glasses

Attention should also be called to Mayer and Havas' tests of *fluorine glasses.* The starting point of these glasses was a boric acid glass which they called "normal glass II," whose analysis is as follows:

	Per cent
Na_2O	18.14
B_2O_3	19.09
Al_2O_3	11.17
SiO_2	51.60
	100.00

The batch mixtures of these fluorine glasses were obtained by the addition of 2.5%, 5.0%, and 7.5% of different fluorides with respectively 97.5%, 95.0%, and 92.5% of "normal glass II." After melting, each fluorine glass was analyzed, and the data submitted by them and reproduced in *Chimie et Industrie* (*loc. cit.*) shows that the "*normal glass II,*" *with different fluorides added, behaves in a quite different manner than the fluorine enamels.* In these glasses *the silica* (SiO_2) *does not undergo any change,* the alkalies and boric acid do not volatilize, and on the contrary,

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[1] See *Chimie et Industrie,* **2,** 872–87 (1923), for complete data.

TABLE VIII

No.	Vogt's glaze	Ground-coats			White enamels		Mixture of normal glass II and							
							CaF_2		Na_2F_2		Al_2F_6		Cryolith	
							2.5%	5%	5%	10%	5%	10%	5%	10%
	1	2	3	4	5	7	8	9	10	11	12	13	14	15
Na_2O	87.85	97.38	102.75	101.31	101.75	96.95	99.87	100.05	99.98	99.94	100.07	100.08	100.03	99.86
K_2O		108.02	103.01	101.14	103.10	89.40	....	....	....	....	....	....	....	....
CaO	101.28	104.58	99.56	100.07	99.72	147.95	98.17	93.65	....	....	....	....	....	....
CoO	....	91.61	104.48	102.65	....	....	....	....	....	....	....	....	....	....
MnO	....	104.72	103.45	101.35	....	....	....	....	....	....	....	....	....	....
B_2O_3	....	96.63	97.50	97.00	93.10	96.30	100.20	100.50	100.19	100.4	100.7	101.56	100.19	100.58
Al_2O_3	98.75	100.25	102.87	101.18	102.01	112.25	99.95	100.01	99.95	100.06	99.77	99.50	99.96	100.00
SiO_2	100.72	99.93	99.13	99.39	98.99	98.61	100.05	100.45	100.07	100.03	100.07	100.11	100.07	100.04
F_2	....	79.87	75.95	78.00	88.13	83.85	67.20	64.50	84.25	85.30	62.80	63.80	85.60	84.00
$-O$	....	79.87	75.95	78.00	88.13	83.85	67.20	64.50	84.25	85.30	62.80	63.80	85.60	84.00

the latter *undergoes an increase* that we cannot explain. It may be occasioned by an erroneous calculation, or an inaccurate analysis, but whatever the cause, these tests *prove that there is no formation of silicon tetrafluoride*, and that the fluorine (F_2) vanishes in molecular form.

In order to see how the different compounds are affected in the smelting process, a study should be made of Table VIII. The values in this table represent the per cent of each constituent remaining in the enamel, *considering the amount which should theoretically be there as 100%.*

The small number of tests considered, and their inaccuracy do not allow setting up any definite rule which will express the change of enamel constituents as a function of the enamel composition. Our general conclusions, which follow, do not, therefore, claim to lay down a law.

Conclusions

The data which have been submitted demonstrate that *the volatilization of fluorine depends chiefly on thermal conditions, i. e.*, the smelting temperature, and its duration (compare No. 5 and No. 7)—then, *second, on the enamel composition* (compare No. 3 and No. 9) and *last, on the fluoride added* (compare No. 9 and No. 14).

The quantity of fluorine remaining in the ground coats varies from 78% to 80% of the original quantity. In white enamels it varies from 84% to 88%. It is true that the volatilization of fluorine increases in more siliceous enamels, but not owing to the increase of silica, which was supposed to be transformed into silicon tetrafluoride, but because the silica increase, by augmenting viscosity and decreasing fusibility, requires a higher and more prolonged smelting temperature.

The rôle which boric acid (B_2O_3) plays is strange, for it shows an *increase* in *glasses* containing fluorine and a *decrease* in *enamels*. In ground coats there remains 96.6% to 97.5%, while 93.0% to 96.3% remains in white enamels. We cannot give any rule for these changes, but it is evident that the volatilization of boric acid *diminishes* when fluorine *increases*.

There can be no scientific explanation for the 99.6% to 148% variation of calcium oxide (CaO). The variations of the alkalies in the enamels is quite suspicious, especially in view of the fact that in the glasses containing fluorine the alkalies showed great stability.

Silica changes least of all in these analyses. It does not change in the fluorine glasses, nor in Vogt's glaze, which had the highest percentage of silica of any of the compositions. In all cases there remains from 98.61% to 99.93% of the silica theoretically there. *The maximum loss of silica (1.39%) which we have found, would, at the most, allow of the formation of only 2.4% of silicon tetrafluoride (SiF_4) for 100% of melted enamel, which corresponds to but 10.8% of the total loss of fluorine.*

This ought, at least, *to put in grave doubt, the theory that fluorine vanishes as silicon tetrafluoride.*

Perhaps before concluding, we should here take cognizance of the fact that fluorine may combine with boron and vanish in the form of boron fluoride (BF_3), as suggested by Mayer and Havas and referred to earlier in this paper. Boron combines with fluorine according to the equation:

$$B + F_3 = BF_3$$
$$11 + 57 = 68$$

from which we may see that $^{11}/_{57}$ parts by weight of boron are required to combine with 1 part by weight of fluorine.

If we calculate from the loss of fluorine the amount of boron which would be lost by such a reaction taking place on some of the enamels from Table VIII, we obtain values as given below:

TABLE IX

No. of enamel	2	3	4	5	7
Amt. boron by analysis	96.63	97.50	97.00	93.10	96.30
Amt. boron by calculation	96.12	95.36	95.76	97.71	96.88

These values are so closely connected that one would be tempted to conclude, that, at least in the ground coats examined, all of which contain B_2O_3, that *the volatilization of fluorine takes place almost entirely under the form of boron fluoride.* The proof of such a conclusion, would, of course, rest almost entirely upon the gas analysis.

DISCUSSION

By J. E. Hansen[1]

It is unfortunate that Mr. Musiol does not substantiate his rather novel conclusions as stated in his paper on "Exact Notions of Fluorine Enamels" with *chemical data*, showing either the *absence* of silicon tetrafluoride in the by-product gases, or the *presence* of definite fluorine compounds of different nature, rather than basing his conclusions on a "mathematical proof," in which there is the possibility of a fallacy, as will be shown below.

The following figures give the analysis of a ground coat enamel batch before smelting (Analysis "A"). If it is *assumed that all the fluorine* (F_2) *in the batch is driven out as silicon tetrafluoride* (SiF_4), and that there is no fire loss of other constituents, we derive the analysis "B," which, when corrected for the loss of SiF_4 and multiplied by the proper factor to give 100%, gives us analysis "C." This analysis would show a difference in SiO_2 from the original batch of 0.4%, or less than 0.8% of the silica present, with other constituents higher, *and yet all the* F_2 *"disappeared" as* SiF_4. However, if we assume a loss from the batch of 0.35% B_2O_3 and 0.35% Na_2O, as could easily take place according to Poste and Rice,[1] we find that our analysis, when corrected to total 100% (analysis "Cx"), gives us a value for SiO_2 which is identical with that in the raw batch analysis, and which, on the surface, would indicate "no loss in SiO_2."

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[1] Industrial Fellow, Mellon Institute of Industrial Research, University of Pittsburgh, Pittsburgh, Pa.

Certainly in this case no one would say that "since no silica (SiO_2) was lost there was no formation of silicon tetrafluoride (SiF_4)," especially since the formation of SiF_4 was the assumption on which the calculations were made. Neither will it be necessary to suggest clerical errors or an inaccurate analysis to account for increases in other constituents of the analysis, for when one constituent disappears from the analysis, all others must increase in a constant ratio if the analysis is to total 100%.

The writer does not contend that the fluorine left the enamel batch in the form of silicon tetrafluoride, for he has done no research on the subject to prove or disprove it, but the offering of the above figures points out that a mathematical explanation of an analysis of the smelted enamel cannot prove in what form the constituents, which were driven off, left the batch. Only an analysis of the gases which left the enamel could show that.

Together with Mayer and Havas, and with Mr. Musiol, the writer admits the great probability that the fluorine may have been driven off in combination with boron, as boron fluoride. The reaction in such a case might be of the type

$$3CaF_2 + B_2O_3 = 3CaO + 2BF_3.$$

However, issue can be taken with Mr. Musiol on his statement in connection with the discussion of Mayer and Havas' "fluorine glasses" that "these tests prove that there is no formation of silicon tetrafluoride, *and that the fluorine* (F_2) *vanished in molecular form*" (the italics are the writer's). Any reaction whereby fluorine can be driven off as F_2 from fluorspar, cryolite, sodium fluoride, or aluminum fluoride by heating, is, as far as the writer can learn, new to ceramics and chemistry, and the statement ought to be substantiated by a more full proof.

Fluorine is known to be one of the most active, if not *the most active* element known to chemists. Crystallized silicon and amorphous boron, when thrown into fluorine gas, take fire and burn, with the formation of fluorides. The alkali metals and the alkaline earth metals also ignite in

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[1] *Jour. Amer. Ceram. Soc.*, **1**, 221–234 (1918).

Analysis	**"A" Per cent**
SiO_2	50.90
B_2O_3	13.85
Al_2O_3	5.70
Na_2O	17.40
K_2O	1.69
CaO	0.16
CaF_2	7.56
NiO	0.57
MnO	1.03
CoO	1.14
	100.00

Assume all F_2 volatilized as SiF_4 →

$$\underset{156}{2\,CaF_2} + \underset{60.3}{SiO_2} = \underset{112}{2CaO} + \underset{104.3}{SiF_4}$$

$$\frac{60.3}{156} \times 7.56(\%\ CaF_2) = 2.93 \text{ loss in } SiO_2$$

$$\frac{112}{156} \times 7.56(\%\ CaF_2) = 5.43 \text{ gain in CaO}$$

$$\frac{104.3}{156} \times 7.56(\%\ CaF_2) = 5.06\%\ SiF_4 \longrightarrow$$

	"B" Per cent
SiO_2	47.97
B_2O_3	13.85
Al_2O_3	5.70
Na_2O	17.40
K_2O	1.69
CaO	5.59
NiO	0.57
MnO	1.03
CoO	1.14
	94.94
SiF_4	5.06
	100.00

Divide by .9494 →

	"C" Per cent
SiO_2	50.50
B_2O_3	14.60
Al_2O_3	6.01
Na_2O	18.34
K_2O	1.78
CaO	5.89
NiO	0.60
MnO	1.08
CoO	1.20
	100.00

Arbitrarily assume a loss of 0.35% B_2O_3 and 0.35% Na_2O, as per Poste and Rice, *Jour. Amer. Ceram. Soc.*, **1**, 221–234, (1918).[1]

	"Bx" Per cent
SiO_2	47.97
B_2O_3	13.50
Al_2O_3	5.70
Na_2O	17.05
K_2O	1.69
CaO	5.59
NiO	0.57
MnO	1.03
CoO	1.14
	94.24
SiF_4	5.06
Loss $Na_2O + B_2O_3$	70
	100.00

Divide by .9424 → to make total = 100%

	"Cx" Per cent	
SiO_2	50.90	same SiO_2 content as in Analysis "A"
B_2O_3	14.32	
Al_2O_3	6.05	
Na_2O	18.10	
K_2O	1.79	
CaO	5.93	
NiO	0.61	
MnO	1.09	
CoO	1.21	
	100.00	

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[1] Of course there are other smelting losses besides B_2O_3 and Na_2O, but it is not necessary to include them to prove the point in question—that all F_2 could go off as SiF_4, and still SiO_2 be equal to or even higher in the smelted enamel than in the raw batch.

the gas. If fluorine gas escapes *as such*, from a bath of molten enamel, it is a phenomena hitherto unknown by chemists.

Mr. Musiol has supplied us with that celebrated quotation of Lavoisier's, "Nothing is lost, nothing creates itself," but he does not explain where he gets the oxygen which replaces the fluorine of the fluorspar, or unites with the Ca of the CaF_2 to form CaO. Truly, there is always a certain amount of sodium or potassium nitrate (an oxidizing agent) in an enamel batch mixture, but, as a rule, not enough to supply the oxygen needed to form CaO from the Ca present in CaF_2. The writer is at a loss to explain where such oxygen comes from, unless it be from one or more of the following type "double decompositions:"

$$2RF_2 + SiO_2 \longrightarrow 2RO + SiF_4$$
$$3RF_2 + B_2O_3 \longrightarrow 3RO + BF_3$$

or

$$2R_2F_6 + 3SiO_2 \longrightarrow 2R_2O_3 + 3SiF_4$$
$$R_2F_6 + B_2O_3 \longrightarrow R_2O_3 + 2BF_3$$

EUROPEAN PRACTICE IN THE MANUFACTURE OF ENAMELED CAST IRON WARE

By Julius Grunwald

The following review of European practice in the enameling of cast iron ware, particularly as employed in Austria and Germany, will be of interest to the enamelers in the United States. The methods used in these European countries differ considerably from the general practice in American plants.

Manufacture of Cast Iron Utensils

In the manufacture of thin wall castings to be enameled, there are two principal conditions to be considered in calculating the cupola charge; (1) the softness of the iron required, and (2) the necessary fluidity of the iron. Both conditions must be carefully considered in mixing the iron. The softness of the iron is necessary in order to avoid cracking of the casting, the walls being only $^1/_8$ of an inch thick. The greatest fluidity of the iron is necessary to effect the pouring of the thin ware and hot iron is absolutely essential.

It is not difficult to obtain proper mixtures of iron for this ware. The castings do not require any special or expensive grade of pig iron. To obtain the required degree of softness in the iron it is best to use good haematite iron with about 2.5% silicon, 1.7–1% manganese,

Table I

Type of pig iron	Silicon, per cent	Manganese, per cent	Phosphorus, per cent	Sulphur, per cent	Copper, per cent
Haematite	2.0–3.0	below 1.3	below 0.1	below 0.04	......
Foundry pig iron No. I	below 2.5	below 1.0	below 0.6	below 0.04	......
Foundry pig iron No. III					
a. Rhineland-Westphalia	1.0–2.5	below 1.0	below 0.9	below 0.06	......
b. Siegerlander	1.8–2.0	below 1.0	below 0.9	below 0.06	......
Puddled iron of best quality					
a. Rhineland-Westphalia	.....	2–3.0	0.3–0.5	below 0.08	below 0.35
b. Siegerlander	.....	3.0–5.0	0.3–0.5	below 0.08	below 0.35
Steel iron					
a. Rhineland-Westphalia	.....	4.0–6.0	below 0.1	below 0.04	below 0.30
b. Siegerlander	.....	4.0–6.0	below 0.1	below 0.4	below 0.40
Thomas-iron					
a. Mn	.....	below 2.0	1.8	0.12	......
b. M.M.	.....	about 1.5	1.8	0.12	......
c. C.M.	.....	below 1.0	1.8	0.12	......

0.06–0.09% phosphorus and 0.03–0.05% sulphur. It is the rather high percentage of silicon of the haematite iron that gives the required softness to the iron and insures a gray fracture even in thin-walled castings. In order to obtain the highly fluid condition that is necessary, pig iron with a high percentage of phosphorus is used. For this purpose special types of Luxembourg pig iron have been introduced in Germany, these having a large percentage of phosphorus. The composition of the various pig irons employed are given in Tables I and II.

TABLE II

Type of pig iron	Total carbon	Si	Mn	P	S	Cu
Foundry pig iron No. I Dill-Lahn	3.89	0.62	0.64	0.67	0.013	0.004
Upper Silesia	3.42	2.92	0.76	0.48	0.042	0.030
Foundry pig iron No. III Lorraine-Luxembourg	3.58	1.17	0.41	1.71	0.014	0.003
Foundry pig iron Kupferhutte (charcoal-pig iron as a substitute)	4.02	0.84	0.29	0.06	0.052	0.082
Charcoal pig iron (gray)	3.41	1.41	0.39	0.73	0.092	0.011
Charcoal pig iron Siegerlander	3.0–4.0	1.0–3.0	0.3–0.5	0.20	trace	trace
Bessemer pig iron	3.76	2.52	3.90	0.07	0.03	trace
Spiegel iron Siegerlander	4.0–5.0	0.3–0.5	6.0–30.0	0.06	0.1	0.2–0.3
Ferro-manganese	5.5–7.0	0.1–1.5	below 85	0.18	trace	0.02–0.3
Ferro-silicon	1.0–1.5	8.5–15	1.0–4.0	0.08	0.02	0.02–0.3

Before giving the proper mixtures it is necessary to know the analysis of the finished castings. A typical composition is shown in Table III.

TABLE III

COMPOSITION OF TYPICAL GERMAN CASTINGS

	Per cent
Silicon	2.4
Manganese	0.5–0.7
Phosphorus	1–1.1
Sulphur	0.05–0.07

The author suggests the following range of compositions as most satisfactory for castings to be enameled.

	Per cent
Carbon	3.5
Silicon	2–2.5
Phosphorus	1–1.4
Manganese	0.5–0.7
Sulphur	0.05 to 0.08 at most

Since an excess of sulphur makes the iron refractory, a coke with the smallest percentage of sulphur is necessary for proper smelting of the iron. In order to make the sulphur of the coke inactive or to prevent the iron from being enriched by the sulphur of the coke, care must be taken to distribute the limestone uniformly on the coke so that the sulphur may be combined and removed with the slag. Excess sulphur also decreases the fluidity of the iron and causes blistering of the enamels. The addition of ferro-silicon of high percentage cleans the metal bath and softens the iron. Typical iron mixes are shown in Tables IV, V, and VI.

TABLE IV

MIX FOR BATH TUBS, 1/4–3/8″ THICK

	Per cent
Haematite	30
Luxembourg III	35
Siegerlander white	5
Light scrap castings	30

TABLE V

MIX FOR ENAMELED HOUSEHOLD UTENSILS

	Per cent
Luxembourg III	15
German III	20
English	20
Scrap castings	20
Soft cast iron scrap	25

TABLE VI

TYPICAL MIXES OF IRON IN GERMANY

	a Per cent	b Per cent
Haematite iron	30	20
Luxembourg iron III	35	35
Cast iron scrap	..	20
Foundry scrap	35	25

In order to obtain good castings for enameling purposes pulverized graphite must not be used in the molds. The use of pulverized talc or a mixture of ground charcoal and clay is recommended.

Preparation of Castings for Enameling

Pickling is an absolute necessity. After having been heated to a dull red in the muffle furnace at about 850°C (1560°F) without nesting, the goods are pickled in sulphuric acid of 10° Baumé for about 40 minutes. By introducing steam the pickling bath is heated to 60–70°C (140–160°F). The goods are then rinsed in water to remove the excess of acid, after which they are scrubbed by means of wire brushes or combs, sand being used only when the latter are not satisfactory. The castings are rinsed again and then placed for a moment in a boiling soda solution containing about 3–4% of soda. Finally they are quickly and thoroughly dried on drying-boards as is done with sheet ware. Should there still be some dark spots remaining they are to be removed by means of a file. Large stains must be removed by further pickling and scrubbing. The pickled goods must show a uniform, gray, silvery, metallic surface. The castings are now ready for the application of the ground coat.

The following batch is typical of a suitable ground coat frit for cast iron utensils: flint 14, borax 4, fluorspar, 4.

These materials are carefully mixed, sifted and then placed in cast iron pans, 20″ x 12″ x 4″. The inside of the pan is first coated with a wet paste of clay $^1/_4$ inch thick. The pan thus prepared is filled with the ground mass just below the rim, and it is then placed in the muffle furnace for 2 to 3 hours (the exact time has to be found by experience according to local conditions.) Generally the mass is kept fritting until ebullition caused by the escaping of the water of crystallization of the borax has ceased and a smooth frit of a highly porous character is obtained. Three test batches fritted 1, 2, and 3 hours should be ground separately. Fritting in the muffle furnace is done best at a time when it is not being used otherwise. The pan is withdrawn and entirely cooled. Then the fritted mass is broken with the aid of a small hammer and removed. Special care should be taken to reject pieces of clay or iron scale which may adhere to the frit. The frit thus obtained is ground in the wet mill together with the following ingredients: Frit 12 parts, heated quartz 4 parts, clay for enameling purposes $1^1/_2$ parts, and water 6–7 parts. This batch is ground to pass a 40-mesh sieve.

Before applying the ground coat upon the goods, these are wiped with a slightly moistened rag, especially the bottom (in order to prevent the layer of enamel deposited there becoming too thick). The ground mass is applied to smaller articles by slushing in a manner similar to that used for sheet metal. Too thick a layer of ground coat must be avoided as well as too thin a layer. Experience will lead to the proper thickness of enamel to be applied. Drying must be done immediately in the drying stove to prevent rusting of iron.

The ground coat ware is burned at the same temperature as for sheet metal, this temperature being 900–950°C (1650–1740°F). Burning the ground mass requires special attention as production of good ware is dependent upon it. Burning too sharply will cause what is called "over burning;" under burning may cause cracking of the ground coat after cooling. A criterion of proper burning is that the fired ground coat cannot be scratched with the finger nail.

The cover coat is applied in the same way and as a rule is of the same composition as those used on sheet steel. Cast iron utensils require only one cover coat.

If there are larger pieces of rejected ware, it is advisable in order to reclaim the casting to remove completely the ground coat by sand blasting. If only a part is damaged these areas can be coated with a ground mass and enameled after local sand blasting. In this way it is possible to secure second-class goods at least.

VIENNA, AUSTRIA

THE RELATION OF TEXTURE AND COMPOSITION OF CLAYS[1]

By Frank F. Grout[2]

ABSTRACT

Twelve Minnesota clays of diverse origin and character, which had been analyzed, were separated mechanically into five fractions, from coarse sand to fine clay, and each fraction was analyzed.

Silica is at a maximum in the fine sand portion of most clays. Alumina, iron oxides and potash are at a minimum in this portion, but while they rise a little in the coarse sand, they reach their highest proportion in the fine clay portion. Other oxides show less regularity.

An estimate of the minerals is made on the basis of all available information, though it may never be possible to tell how much colloidal material is present, making the calculation inaccurate. It seems clear that kaolinite and limonite are larger in clays than in silts, while quartz and carbonates are smaller. Others are less regular.

A detailed comparison of "fluxing constituents" and the temperatures of viscous fusion, led to the suggestion that the behavior of a clay in firing is determined not so much by the total fluxes as by the proportion of fluxes in the fine clay fraction. If this proves to be true, as it seems to be in the Minnesota clays, it should be possible to foretell more accurately than heretofore, the thermochemical and physical changes, on the basis of preliminary laboratory work. Not only the firing of the clay itself, but its effect on admixtures of other clays and its modification by washing can be fairly well estimated from a combined mechanical and chemical test.

Introduction

The determinations reported in this paper were made with a view to finding the distribution of the common elements in the portions obtained by mechanical separation of the several sizes of grains in a series of clays. Such results may (1) aid the petrographer in estimating the minerals of clays of several types, (2) aid the clay users in determining whether a washing process or a mixture of materials will improve a clay, and (3) possibly furnish a basis for more accurate correlation of the behavior of a clay in firing with its analytical composition.

It has long been understood that chemical analysis alone is not a satis-

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[1] Received Nov. 29, 1923.

[2] Much of the work here reported was done by the writer in connection with the preparation of a report by the Minnesota Geological Survey on the clays and shales of Minnesota. (Minn. Geol. Surv., *Bull.* **11** (1914). See also U. S. Geol. Surv., *Bull.* **678** (1919). Credit is there given for a few analyses made by assistants.) Hearty thanks are due to the Survey for the privilege of using the samples collected through the state. Some of the analyses of "whole clay" were published in that report. Further tests have been made partly by the writer and partly by student chemists, S. F. Darling, Douglas Manuel, and C. W. Sanders, working under a grant from research funds of the Minnesota Graduate School. Grateful acknowledgments are here given for that assistance. Where doubt arose as to any student determination, the writer has run check analyses if material was available, and takes all responsibility for the approximate correctness of the data. The lack of agreement between the whole clay and sum of fractions is not much greater than is to be expected in chemical work by different student chemists.

factory index of the behavior of a clay. Purdy and Moore say:[1] "While thermochemical and physical changes follow definite laws they cannot be foretold by any analysis of primary causes...now known." It is with a hope of approaching such a forecast that the present work has combined a study of *texture and chemistry*. More data are needed along the same lines before we can be confident of the fundamental value of the scheme, but it is suggested for further work. The combined analyses are, of course, too expensive to consider as a method of daily check on factory operations. Nevertheless such methods may not be in any way too difficult (if as reliable as they seem) to use in predicting the value of a large deposit under conditions of washing or admixture of other clays.

Many men have called attention to the importance of fineness of grain in ceramics, from the time of Seger to the present day. The publications of the AMERICAN CERAMIC SOCIETY contain excellent articles on the topic.[2] Some of the behavior of a clay also depends on the form of combination of the constituents. It seems, however, that if a clay has a certain proportion of fine and coarse grains, and each portion has a definite composition, another clay with the same mechanical analysis and the same chemical composition in each fraction, ought to behave similarly in the fire. The mineral composition may still affect the behavior to some extent, but in the finer sizes such as make up many clays, reaction would take place very rapidly, and once reaction occurs, the composition would determine its behavior.

Only a little work of this sort has been done on clays. A preliminary study of the relation of fineness to composition was made by the writer in 1905 on a composite sample of West Virginia clays.[3] While the results in such a composite are not of direct ceramic value, several points of general application were noted. The United States Bureau of Soils has made a number of similar determinations on soils,[4] but the proportion of silt and clay (not always reported) is smaller in loams than in most clays; and the finer sizes were not separated in their work, whereas in clays the most significant points depend on the separation of fine and coarse clay and silt. Sven Odén analyzed a series of fine clay fractions of a Swedish glacial deposit.[5] Widman tested similarly the fractions of a weathered granite.[6]

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[1] R. C. Purdy and J. K. Moore, *Trans. Amer. Ceram. Soc.*, **9**, 314 (1907).

[2] Purdy and Moore, *op. cit.* See also H. Ries, *Trans. Amer. Inst. Min. Eng.* (1903).

[3] West Va. Geol. Surv., **3**, 60–62 (1906).

[4] L. A. Steinkoenig, "Distribution of Certain Constituents in the Separates of Loam Soils," *Jour. Ind. Eng. Chem.*, **6**, 576 (1914).

[5] A series of papers reported in *Bulletins of the Geol. Inst. of Upsala*, **15** and **16** (1916–1919).

[6] Widman, R., *Bull. Geol. Inst. Upsala*, **8**, 184 (1908).

Description of Samples

The samples for this test were selected from several hundred clays collected by the writer and assistants in several parts of Minnesota. The nature of the deposits is indicated in the tables. They range geologically from pre-Cambrian residual clay through Ordovician and Cretaceous shales to Pleistocene and Recent clays. Chemically some are rich in iron, some in lime, some in silica, some in alkalies. No effort was made to choose the highest grade clays, though nearly all are serving some ceramic purpose. The use of the clay is also given in the tables. Details of the behavior in manufacture and firing are given at greater length in the Survey bulletins.

Preparation of Separates

Twenty-gram samples were shaken in bottles with water to which a few drops of ammonia had been added. Lumpy shales were in certain cases gently rubbed with a rubber tipped pestle. The disintegrated sludge was then washed through sieves and centrifuged approximately as described in *Bulletin* **84** of the United States Bureau of Soils. The diameters were checked by microscopic measurement and few grains in any separate varied from the following.

A.	Fine clay[1]	0.0 to .001 mm.	D.	Fine sand	.05 to .5 mm.
B.	Coarse clay[1]	.001 to .005 mm.	E.	Coarse sand	over .5 mm.
C.	Silt	.005 to .05 mm.			

Most of the separations were made by the writer; a few were made by students under his direction. The results in a check test are essentially similar to those obtained by the United States Bureau of Standards.

Methods of Analysis

The determinations were made by methods based on those by Hillebrand,[2] but modified slightly where material was scanty. Too much organic matter is present in most clays to allow a reliable estimate of ferrous oxides. In most cases also, on account of the organic matter, loss on ignition is reported rather than combined water, though the error in estimate of water is believed to be small; organic matter may be of small weight and still have a reducing action.

Silica, iron oxide, alumina, titanium oxide, lime, and magnesia were determined in a half-gram sample. Moisture, loss on ignition, and in

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[1] It is perhaps an error to class as "clay" all the grains less than .005 mm. in diameter, but the term is retained here as the common usage. The error of several methods of estimating "clay substance" in clays was shown in the clay report of the West Virginia Geol. Surv., **3,** 26.

[2] U. S. Geol. Surv., *Bull.* **700.**

TABLE I

Clay No. 1. Gray drift, Hutchinson, Minn. Commercially washed to remove pebbles and used for brick and drain tile.

		Fractions				
	Whole clay	Coarse sand 17.1%	Fine sand 24.7%	Silt 38.6%	Coarse clay 12.0%	Fine clay 7.6%
Silica	58.85	53.26	75.72	53.20	46.44	47.0
Alumina	7.25	6.48	7.16	8.76	14.82	16.5
Iron oxides	4.97	2.54	1.72	3.27	7.52	10.5
Magnesia	3.45	5.00	1.76	5.00	3.16	3.0
Lime	9.42	14.40	6.56	12.04	8.84	4.5
Soda	1.37	1.34	.92	2.14	1.06	.9
Potash	1.76	1.66	1.44	2.08	2.38	2.5
Ignition	2.10	15.22	1.24	3.29	5.01	9.0
Carbonic acid[1]	9.10		4.00	8.34	6.85	
Moisture[2]	2.10	.32	.06	1.04	3.60	4.6
Titania	.36	.18	.14	.61	.92	.8
	100.73	100.40	100.72	99.77	100.60	99.3
Fluxes	*21.0*	*25.0*	*12.4*	*24.5*	*23.0*	*21.5*

[1] CO_2 estimated on small amounts of material. Where estimated, it is subtracted from total loss on ignition. Analysis of whole clay in U. S. Geol. Surv., *Bull.* 678 has a typographical error.

[2] Sands had visible quartz, orthoclase, dolomite, trap rock, etc. Clays slightly coherent as if colloidal.

TABLE II

Clay No. 2. Cretaceous clay, clay bank near Red Wing, Minn. Commercially washed to purify it, and used for stoneware.

		Fractions				
	Whole clay	Coarse sand 1.0%	Fine sand 6.5%	Silt 49.8%	Coarse clay 16.0%	Fine clay 26.7%
Silica	69.92	37.0	91.28	79.16	53.32	45.85
Alumina	17.39	1.7	.77	11.59	29.24	32.96
Iron oxides	1.68	47.4	5.17	1.68	2.46	2.62
Magnesia	1.11	2.0	.73	.97	1.16	1.73
Lime	.60	1.7	.78	.46	1.32	1.04
Soda	.07	N. d.	.12	.04	1.04	1.28
Potash	2.25	N. d.	.90	1.46	2.48	1.79
Ignition	5.45	9.6	.84	3.02	7.32	9.02
Moisture	1.10	.9	.00	.08	1.08	3.52
Titania	.63	N. d.	trace	1.49	1.46	.74
	100.20		100.59	99.95	100.88	100.55
Fluxes	*5.7*	*51.1*	*7.7*	*4.6*	*8.5*	*8.5*

Sands had visible limonite (concretionary), quartz, muscovite, and a little black mineral.

Clays formed a crust or scale as if largely colloidal.

some cases alkalies, were determined in a second half-gram sample. Where CO_2 was abundant it was determined on a gram sample and the amount

TABLE III

Clay No. 3. Decorah (Ordovician) shale, St. Paul, Minn. Used for fancy building blocks and brick and tile.

		Fractions				
	Whole clay	Coarse sand .7%	Fine sand 1.5%	Silt 46.8%	Coarse clay 13.2%	Fine clay 37.8%
Silica	56.35	60.0	61.8	57.20	52.20	50.30
Alumina	18.63	7.0	10.3	19.78	23.88	22.02
Iron oxides	6.19	1.8	3.0	5.20	5.80	6.54
Magnesia	2.97	.4	2.3	1.88	2.84	3.32
Lime	.96	10.9	5.4	1.45	.96	1.05
Soda	.25	.2	.8	1.34	.70	.68
Potash	7.37	4.8	4.9	6.90	6.62	6.70
Ignition	4.81	10.8	5.3[1]	2.12[1]	4.90	5.94
Carbon dioxide	N. d.	Large	1.9	1.78	None	None
Moisture	2.41	1.5	2.9	1.40	1.80	2.64
Titania	.65	.2	.5	.72	.92	.78
	100.59	97.6	99.1	99.77	100.62	99.97
Fluxes	*17.7*	*18.1*	*16.4*	*16.8*	*16.9*	*18.3*

Sands show calcareous fossils, quartz and limonite.

[1] "Ignition" has been reduced by amount of carbon dioxide determined.

TABLE IV

Clay No. 4. Cretaceous shale, Springfield, Minnesota.[1] Used for hollow brick and tile.

		Fractions				
	Whole clay	Coarse sand 4.0%	Fine sand 16.0%	Silt 76.8%	Coarse clay 2.1%	Fine clay 1.1%
Silica	64.08	65.	62.16	67.84	44.9	33.
Alumina	17.48	1.7	16.12	14.54	22.2	18.
Iron oxides	5.03		6.16	4.80	6.3	5.
Magnesia	1.42	1.	.51	.82	2.6	4.
Lime	1.00	3.	1.76	.96	4.0	10.
Soda	.20	N. d.	1.81(?)	.14	N. d.	N. d.
Potash	1.74	N. d.	1.34	1.70	N. d.	N. d.
Ignition	7.12	14.	7.80	6.78	16.0	20.
Moisture	1.00	N. d.	1.40	.56	1.3	6.
Titania	1.19	N. d.	1.07	1.22	1.2	1.
	100.26		100.13	99.36		
Fluxes	*9.5*	*9.+*	*11.6*	*8.4*	*13.+*	*19.+*

Sands show quartz, black sand, and shale lumps.

Clay contains some carbonaceous matter.

[1] This is a clay bank on the other side of Springfield from that of which analysis is given in U. S. Geol. Surv., *Bull.* **678**, p. 134.

subtracted from the loss on ignition. Each table reports as "fluxes" the sum of the oxides of iron, magnesium, calcium, sodium and potassium.

TABLE V

Clay No. 5. Residual clay from biotite schist, Bowlus, Minnesota. Not used.

		Fractions				
	Whole clay[1]	Coarse sand 18.5%	Fine sand 41.7%	Silt 38.7%	Coarse clay 1.0%	Fine clay .1%
Silica	57.20	36.70	65.12	56.06	40.	....
Alumina	18.23	35.41	14.59	21.80	17.	....
Ferric oxide	5.45	8.22	4.71	7.41	12.	....
Ferrous oxide	5.03	8.14	3.61			....
Magnesia	1.02	1.89	1.00	1.43	4.	....
Lime	.72	.24	.16	.43	5.	....
Soda	.61	1.23	.46	.94	N. d.	....
Potash	.98	1.37	.68	.86	N. d.	....
Ignition	8.20	6.38	8.58	9.62	18.	....
Moisture	.24	.00	.36	.92	1.	....
Titania	1.52	.97	1.21	1.21	1.	....
	99.20	100.55	100.48	100.68		
Fluxes	*13.8*	*21.1*	*10.6*	*11.1*	*21.*	

Sands show staurolite, chlorite and quartz.

[1] Modified from that published in U. S. Geol. Surv., *Bull.* 678, to show *ferrous* iron, and corrected amounts of moisture and combined water.

TABLE VI

Clay No. 6. Red glacial drift, Coon Creek, Minnesota. After passing rolls, used for medium vitrified brick.

		Fractions				
	Whole clay	Coarse sand 5.5%	Fine sand 5.1%	Silt 47.5%	Coarse clay 24.6%	Fine clay 17.3%
Silica	60.49	67.57	86.04	64.94	53.06	46.70
Alumina	14.39[1]	15.53	6.90	12.46	19.85	25.26
Iron oxides	6.03[1]	4.00	1.28	3.97	5.39	6.34
Magnesia	3.68	2.12	1.23	4.26	5.34	2.56
Lime	3.87	3.34	1.90	3.40	3.28	3.04
Soda	2.17	2.20	.69	2.04	1.10	2.06
Potash	2.53	1.20	1.37	2.43	2.32	1.92
Ignition	5.90	2.40	.82	4.98	7.61	7.72
Moisture	1.94	.34	.02	.42	1.44	3.92
Titania	.42	1.67	.30	1.11	1.08	1.12
	101.42	100.37	100.55	100.01	100.47	100.64
Fluxes	*18.±*	*12.9*	*6.5*	*16.1*	*17.4*	*15.9*

[1] Corrected from the results shown in U. S. G. S., *Bull.* 678.

Sands show quartz and trap rock.

Clays somewhat scaly as if colloidal.

TABLE VII

Clay No. 7. Glacial laminated clay from red drift, St. Croix River, Pine County, Minnesota. Not now used.

				Fractions		
	Whole clay[1]	Coarse sand trace	Fine sand .3%	Silt 42.0%	Coarse clay 29.7%	Fine clay 28.0%
Silica	56.85	....	76.0	63.38	54.14	47.00
Alumina	14.87	....	13.0	13.45	17.58	18.16
Iron oxides	7.40	....	3.0	4.81	8.14	10.88
Magnesia	4.49	....	1.0	3.46	4.50	5.32
Lime	3.58	....	2.0	4.08	2.44	2.24
Soda	1.31	....	N. d.	1.58	.96	1.22
Potash	2.39	....	N .d.	2.81	2.90	2.88
Ignition	6.60	....	2.5	5.16	7.86	7.08
Moisture	1.80	....	.5	1.14	.34	3.92
Titania	.55	....	.5	.54	.68	.92
		....				
	99.84	....		100.41	99.54	99.62
Fluxes	*19.2*	....	*6.+*	*16.7*	*18.9*	*22.5*

Clay lumps had to be rubbed to break them up. More rubbing might have increased the per cent of fine clay. Clays slightly colloidal.

[1] Not the same sample as the one reported in U. S. G. S., *Bull.* **678,** p. 215.

TABLE VIII

Clay No. 8. Glacial laminated clay from gray drift, North Minneapolis, Minnesota. Used for cream brick and fire proofing.

				Fractions		
	Whole clay	Coarse sand trace	Fine sand .5%	Silt 79.5%	Coarse clay 10.9%	Fine clay 9.1%
Silica	50.65	....	73.2	50.22	44.76	44.66
Alumina	10.25	....	10.3	9.81	14.34	17.21
Iron oxides	4.00	....	.6	3.03	5.08	7.09
Magnesia	4.68	....	2.0	5.77	4.30	2.88
Lime	10.65	....	4.6	12.36	9.88	6.56
Soda	1.44	....	N. d.	1.02	1.30	1.30
Potash	1.96	....	N. d.	1.51	2.15	2.36
Ignition	2.10	....	5.0	1.96	3.92	5.31
Carbon dioxide	12.30	....	.5	13.60	11.50	7.98
Moisture	1.20	....		.44	2.22	3.76
Titania	.52	....	.2	.55	.34	.92
		....				
	99.75	....		100.27	99.79	100.03
Fluxes	*22.7*	....	*7.2*	*23.7*	*22.7*	*20.2*

Sand shows mostly quartz, but a little magnetite, orthoclase, hornblende, calcite, and mica. Clays formed a crust or scale as if largely colloidal.

TABLE IX

Clay No. 9. Loess clay, Preston, Minnesota. Used for building brick (and in foundry sands).

		Fractions				
	Whole clay[1]	Coarse sand .1%	Fine sand .9%	Silt 84.3%	Coarse clay 8.5%	Fine clay 6.2%
Silica	70.50	58.	67.7	74.80	51.28	46.48
Alumina	12.28	N. d.	9.5	11.36	19.06	23.86
Iron oxides	4.06	N. d.	5.3	3.10	7.84	7.96
Magnesia	1.81	15.(?)	2.8	1.42	2.47	2.77
Lime	1.27	8.(?)	2.1	1.78	1.82	1.20
Soda	1.73	N. d.	.1	1.39	.61	.58
Potash	1.95	N. d.	3.7	2.22	1.40	1.07
Ignition	3.88	10.	6.9	2.80	10.10	12.00
Moisture	1.92	1.	1.5	.46	4.28	4.18
Titania	.34	N. d.	.5	.68	.92	.32
	99.74		100.1	100.01	99.78	100.42
Fluxes	*10.8*	*23.±*	*14.0*	*9.9*	*14.1*	*13.6*

Sands show quartz, limonite, and mica.
Clays formed scale as if largely colloidal.

[1] Not the same sample as the one analysed in U. S. G. S., *Bull.* **678,** p. 160.

TABLE X

Clay No. 10. Lake clay, Heron Lake, Minnesota. Used for hollow brick and drain tile.

		Fractions				
	Whole clay	Coarse sand .4%	Fine sand 4.1%	Silt 69.4%	Coarse clay 16.8%	Fine clay 9.3%
Silica	53.94	60.	81.4	56.28	42.42	42.46
Alumina	11.39	19.	7.0	10.80	14.55	19.93
Iron oxides	3.29		1.0	2.24	6.11	10.22
Magnesia	3.47	8.	.8	3.77	2.71	2.90
Lime	9.80	4.	4.5	10.22	12.22	4.87
Soda	2.34	N. d.	N. d.	1.46	1.73	1.45
Potash	.76	N. d.	N. d.	1.35	.99	.92
Ignition[1]	4.16	4.	2.1	3.00	5.58	9.32
Carbon dioxide	8.62	N. d.	N. d.	9.38	10.68	2.42
Moisture	1.64	2.	.3	.90	2.72	5.28
Titania	.65	N. d.	.2	1.00	.84	.65
	100.06			100.40	100.55	100.42
Fluxes	*19.7*	*18.–*	*6.+*	*19.0*	*23.8*	*20.4*

Sands show mostly quartz, with traces of limonite.
Clays formed scale as if largely colloidal.

[1] Carbon dioxide where estimated is subtracted from total loss on ignition.

TABLE XI

Clay No. 11. Swamp clay, Tower, Minnesota. Used without much success for building brick.

		Fractions				
	Whole clay	Coarse sand 4.0%	Fine sand 18.1%	Silt 73.3%	Coarse clay 3.1%	Fine clay 1.5%
Silica	52.92	58.78	48.92	50.52	43.4	1.
Alumina	16.73[1]	16.00	18.16	16.88	19.1	1.
Iron oxides	4.98[1]	4.16	4.90	4.93	8.1	N. d.
Magnesia	3.78	2.96	3.68	6.73	7.0	5.
Lime	5.95	4.95	6.64	5.88	5.7	25.
Soda	.97	2.42	.70	1.45	N. d.	N. d.
Potash	2.32	2.89	3.36	2.90	N. d.	N. d.
Ignition	8.85	6.75	11.60	8.40	11.1	22.
Moisture	3.33	1.12	2.10	2.06	.4	
Titania	.52	.52	.56	.61	.7	N. d.
Sulphuric oxide	....	....	....	....	....	44.
	100.35	100.55	100.62	100.36		
Fluxes	*18.0*	*17.4*	*19.3*	*21.9*	*21.+*	*30.+*

Coarser sizes are clay lumps not broken by a rubber pestle.
The "fine clay" is mostly soluble salts, gypsum.

[1] Corrected from the results published in U. S. G. S., *Bull.* 678.

TABLE XII

Clay No. 12. River clay as recently deposited by the Minnesota River at Le Sueur, Minnesota. Used for red brick.

		Fractions				
	Whole clay	Coarse sand 4.1%	Fine sand 25.7%	Silt 58.5%	Coarse clay 6.0%	Fine clay 5.5%
Silica	62.20	52.0	64.50	61.60	50.90	42.24
Alumina	7.77	9.0	8.12	8.33	14.31	13.82
Iron oxides	4.53	5.3	4.15	2.89	8.19	7.03
Magnesia	3.18	3.5	2.06	4.23	2.69	1.66
Lime	7.21	8.8	7.40	8.30	4.10	9.10
Soda	3.58	2.4	2.10	2.27	2.02	1.22
Potash	1.63	1.1	2.12	1.73	1.90	3.42
Ignition	9.27	13.7	8.30	11.52	11.78	15.82
Moisture	2.15	2.9	.30	.20	3.96	4.90
Titania	.41	.6	.37	.50	.60	.69
	101.93	100.1	99.42	101.57	100.45	99.90
Fluxes	*20.1*	*21.1*	*17.8*	*19.4*	*18.9*	*22.4*

Sands show fragments of wood, shells, quartz, and lumps of shale and other rocks. Clay seems oily rather than colloidal.

TABLE XIII

SUMMARY OF THE RELATION OF TEXTURE TO COMPOSITION IN TWELVE MINNESOTA CLAYS

		Coarse sands	Fine sands	Silts	Coarse clay	Fine clay
Silica	Av.	54.83	71.15	61.29	48.07	40.61
	Max.	67.57	91.28	79.16	54.14	50.30
	Min.	36.70	48.92	50.22	40.00	1.00[1]
Alumina	Av.	13.02	10.16	13.30	18.83	18.97
	Max.	35.41	18.16	21.80	29.24	32.96
	Min.	1.7	.77	8.33	14.31	1.00[1]
Iron oxides	Av.	11.65	3.72	3.94	6.91	7.42
	Max.	47.4	8.32	7.41	12.00	10.88
	Min.	1.8	.60	1.68	2.46	2.62
Magnesia	Av.	4.19	1.66	3.31	3.56	3.19
	Max.	15.00	3.68	6.73	7.00	5.32
	Min.	.40	.51	.82	1.16	1.66
Lime	Av.	5.93	3.65	5.11	4.96	6.24
	Max.	14.40	7.40	12.36	12.22	25.00[1]
	Min.	.24	.16	.43	.96	1.04
Soda	Av.	1.63	.86	1.32	1.17	1.19
	Max.	2.42	2.10	2.27	2.02	2.06
	Min.	.20	.10	.04	.61	.58
Potash	Av.	2.17	2.20	2.33	2.57	2.62
	Max.	4.80	4.90	6.90	6.62	6.70
	Min.	1.10	.68	.86	.99	.92
Ignition	Av.	8.62	5.08	7.05	10.91	12.51
	Max.	14.00	11.60	15.56	18.00	22.00
	Min.	2.40	.82	2.12	4.90	5.94
Titania	Av.	.69	.50	.85	.89	.79
	Max.	1.67	1.21	1.49	1.46	1.12
	Min.	.18	trace	.50	.34	.32
Fluxes	*Average*	*25.6*	*14.1*	*15.9*	*19.2*	*20.7*

[1] Soluble salts.

TABLE XIV

ANALYSES OF WEST VIRGINIA CLAYS SEPARATED BY MECHANICAL METHOD[1]

	Coarse sands	Fine sands	Silts	Coarse clay	Fine clay
Silica	76.63	81.16	70.30	54.54	44.08
Alumina	13.01	9.76	16.04	23.00	28.16
Iron oxides	4.89	2.53	3.84	6.90	8.93
Magnesia	.48	.39	.80	1.02	1.36
Lime	.47	.31	.72	.82	.76
Soda	.00	.56	.45	.29	.00
Potash	.93	1.78	2.14	3.31	3.05
Moisture	.87	.35	.56	1.10	2.80
Ignition	4.40	2.59	4.33	7.79	10.86
Titania	.60	.78	1.08	1.12	.84

[1] Frank F. Grout, W. Va. Geol. Surv., 3, 60–62 (1906).

The writer's work on West Virginia clays is here copied because it corroborates the general conclusions drawn from the Summary Table of Minnesota clays. The separates of different grades of fineness from some sixteen samples of clay were analyzed, with the results shown in the following table. The sizes of grain in each separate correspond to those in the Minnesota samples. These clays have a much lower per cent of fluxes than the average Minnesota clays, but the variation with texture is in the same direction.

Distribution of Elements by Sizes of Grain

The prevailing ideas on this subject of concentration of certain elements in certain sizes of grain have been developed from scant data. Steinkoenig's data for soils[1] and the writer's report based on West Virginia clays[2] can now be somewhat corrected.

Silica is the most abundant oxide in all cases (except the rare "fine clay" with more soluble salt than sediment). The silica, however, is rarely at a maximum in the coarsest size as was supposed. The averages show clearly, as nearly all the individual samples do, that silica tends to concentrate in the fine sand .05 to .5 mm. Coarser particles usually represent unaltered rock fragments with many minerals, or concretions of other minerals than quartz; but the fine sands are the residues of quartz from the well-leached and transported altered rock.

Alumina shows a steady variation to the maximum in fine clay, but a few coarse sands are rich in aluminous minerals such as feldspar and staurolite, and even lumps of shale.

Iron oxides similarly increase from sand to the finest sizes. The high iron content of coarse sand in the Minnesota average, is largely a consequence of a single sample in which limonite concretions are abundant. They are coarse enough to be washed out commercially. Nevertheless the tendency of iron to be high both in the coarsest and finest, is shown by the results of all the work.

Potash averages show a clear tendency to be at a maximum in the finer sizes and most individual samples confirm the conclusion. Exceptions result from occasional coarse feldspars.

Phosphorus is reported by Steinkoenig as most abundant in the smallest grains.

Combined water is at a maximum in the fine clays and is important in the sands only when limonite or shale lumps appear in those fractions.

There are a few cases where the sum of all the "*fluxing ingredients*" is about the same in each of the analyzed fractions as it is in the whole clay.

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[1] L. A. Steinkoenig, *loc. cit.*

[2] Frank F. Grout, W. Va. Geol. Survey, *loc. cit.*

See Nos. 1, 3 and 12. In a much larger number, the "total fluxes" are a larger per cent of the fine fractions than of the coarse. This is probably related to the increase in iron and potash.

This tendency for fluxes to increase led the writer to remark that "the finest sizes are not the purest kaolin." This was possibly incorrect, or at least a poor way to say that the finest sizes are more contaminated with fluxing impurities. Purdy made some calculations to show that kaolinite is concentrated in the fine clays, along with the concentration of fluxes.[1] The decrease in silica allows an increase of both kaolinite and iron and potash.

Lime, magnesia, soda and titanium vary erratically. Lime as fossils and concretions tends to the coarser fraction, but as a mechanical sediment it is often as fine as silt and may be abundant in the clay sizes. Magnesia in dolomite may behave similarly, but as a silicate, more or less hydrous, its behavior is erratic. It shows a slight tendency to be more abundant in the finer sizes. Soda seems wholly erratic in its behavior, possibly in part due to inaccuracy and incompleteness in the chemical work. Titanium is well distributed in all sizes.

Distribution of Elements by Sizes, in Clays of Different Origin

A study of the exceptions to the general rules just given is instructive geologically. It is the residual clay that shows alumina and iron at a maximum in the coarse sand. This is the exceptional case where alumina and iron were present in two minerals—primary chlorite as well as the usual clay minerals.

Another exception to the rule of greater iron content in the finer clays is found in shales that have been subject to concretionary action. In one case limonite and in another pyrite has developed into such masses as to appear in the coarse sand.

If allowance is made for these two types of deposit (residual clay and shale with concretions), there is even a stronger tendency for all clays to fall into simple series; silica at a maximum in fine sands; alumina, iron oxides, potash, and to some extent magnesia showing larger amounts in the finer sizes.

Textures of Clays of Different Origin

The textures of clays studied in Minnesota are fairly represented by this set of mechanical analyses. While the differences are more or less related to mode of formation of the deposit, it may be too early to attempt to give very definite criteria by which origin can be judged from texture.

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[1] R. C. Purdy, "Pyrophysical and Chemical Properties of Paving Brick Clays," Ill. Geol. Surv., *Bull.* **9**, 180–186 (1908).

It should be emphasized, also, that data are limited to clays, not covering the broader field of sediments in general. The noteworthy features are as follows:

The "clay substance" (grains less than .005 mm. in diameter), constitutes a surprisingly small proportion of these clays. Silt is the most abundant fraction. Clays deposited in quiet water have practically no sand, while glacial and residual clays have much. The wind blown loess is especially well sorted, practically all grains being of silt size.[1]

The Minerals of Fine Clay

The usual list of minerals of clays includes kaolinite and those visible in coarser particles. The estimates of other fine-grained minerals are few and need critical review. Microscopic identification is very difficult. The assumption at the basis of a rational analysis is not satisfactory for complex mixtures such as are here studied.

Some few fine clays have so nearly the composition of kaolinite that it is commonly assumed to be present. Most good kaolins, however, are coarser than the "clay fractions" in a mechanical analysis; and a large number of fine clays have not the composition of kaolinite, so that the assumption of the presence of kaolinite is not entirely safe.

Van Hise suggests that some of the water is combined in hydrous minerals such as *zeolites*.[2] Hutchings found that while feldspar (and biotite, chlorite and clastic muscovite) was absent from the fine parts of carboniferous shales, a new micaceous mineral could be detected.[3] Leith and Mead report that shales in general may have chlorite, serpentine and talc, but are more likely to give oxides, carbonates and hydrates; also that potash may be present as sericite, but likely also adsorbed or combined with the finer or colloidal material.[4] They calculate the percentage of such minerals from the average composition of shales. (See Table XV.)

Purdy has made some calculations on the analyses of fine clay in the attempt to determine whether kaolinite is actually present in it.[5] He notes as Merrill has,[6] that the method of mechanical analysis by which fine clays are separated for chemical tests, leaves with the finest fraction nearly all the soluble salts, and the potash or other salts adsorbed by colloids. See clay No. 11, in this work as an extreme case, in which gypsum constituted most of that fraction.

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[1] This was noted in wind blown sands by M. I. Goldman, "The Petrography and Genesis of Sediments," Maryland Geol. Surv. (1916).

[2] C. R. Van Hise, "Treatise on Metamorphism," U. S. Geol. Surv., *Mon.* **47,** p. 893.

[3] W. M. Hutchings, "Clays, Shales and Slates." *Geol. Mag.*, **33,** 310 (1896).

[4] Leith and Mead, *op. cit.*, pp. 77, 78 and 88.

[5] R. C. Purdy, "Qualities of Clays Suitable for Making Paving Bricks," Ill. Geol. Surv., *Bull.* **9,** 182–185 (1908).

[6] *Op. cit.*, pp. 121 and 365.

Still other results have been obtained showing a further difficulty in any attempt to calculate these minerals. The fine clays with particles less than .001 mm. in diameter have no doubt some particles so fine that they are no longer properly minerals but colloidal solutions or gels, with a variety of adsorbed salts. The United States Bureau of Soils has a fairly conclusive demonstration that soils contain inorganic as well as organic colloids such as have long been suspected in clays. These have been isolated and appear to be essentially silicates of iron and aluminum; the small amounts of lime, magnesia, potash and soda may or may not be parts of the colloid.[1]

With so many disturbing factors it may be doubted whether satisfactory mineral diagnosis can be made of the finest clays, but the abundance of fine clays in some deposits makes it desirable to assemble what information is available and make the best estimate possible. It is possible that further studies of mineral solubilities may make an approximate mineral (rational) analysis possible at some future day. Such a method would have to estimate at least eight or ten minerals rather than the three now reported in rational analyses.[2]

An attempt was made to calculate the mineral composition of the silt and clay fractions of the twelve Minnesota clays and Table XV shows the result. The method is open to criticism, but it is hoped that the approximation may be of some interest.

TABLE XV

COMPARISON OF THE CALCULATED MINERALS OF THE AVERAGES OF FINER FRACTIONS FROM MECHANICAL ANALYSES OF TWELVE MINNESOTA CLAYS

	Silt, per cent	Coarse clay, per cent	Fine clay, per cent	Average shale; estimate by Leith and Mead, per cent
Kaolinite and "clay minerals"	7.5	17.0	23.2	10
Sericite and paragonite	16.6	21.2	22.1	18
Quartz	36.7	19.3	13.1	32
Chlorite and serpentine	8.2	10.3	7.3	6
Limonite, hematite (and pyrite)	3.0	5.5	8.0	5
Calcite and dolomite	10.5	7.5	5.7	8
Feldspars	12.6	7.2	7.3	18
Zeolites	3.0	7.5	6.9	..
Titanite and rutile	1.7	2.0	1.7	1
Carbonaceous matter	.2	.9	.6	1
Moisture	.9	1.3	4.1	..

While there is a wide variation in the several samples, the trend is in most cases much the same as in the average, *viz.*, kaolinite and limonite are larger, and quartz and carbonates smaller as the grain is finer. Others are less regular.

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[1] Milton Whitney, "Fundamental Principles Established by Recent Soil Investigations," *Science*, **54**, 350 (1921).

[2] H. Ries, suggested such a possibility, emphasizing micas in his paper on, "The Rational Composition of Clays," *Trans. Amer. Ceram. Soc.*, **9**, 762 (1907).

The whole clays used in this study have an average composition close to average shale, but the fine clay differs a little from either average, having more kaolinite, zeolite and limonite, but less quartz, carbonate and feldspar.

The Amount of Kaolinite in Clays

Based on such assumptions, the calculated kaolinite in the "clay fractions" of twelve Minnesota clays averages about 20%, ranging from 4% to 53%. It would probably be useless to suggest that any ordinary clay had *no* kaolinite. Purdy has calculated that all grades of sizes of clay have kaolinite[1] and in this he is probably right. Some very plastic samples, however, have much less than 10% of kaolinite by calculation.

Thus if shale No. 3 has potash in mineral combination its content of kaolinite must be very small, around 5%. In several cases the kaolinite content would be doubled if most of the potash is considered adsorbed instead of combined, but it is perhaps most probable that only a part of the potash is adsorbed, and at least in the shales it is held so firmly that it is more likely in the form of sericite.

Again, clay No. 7 is so plastic and has so little kaolinite that one is tempted to suggest the presence of nontronite, the ferric kaolinite, instead of iron oxides, to explain its plasticity.

Finally, whether these assumptions are approved or not, the data indicate what has occasionally been noted before, that clay should not be defined so as to give an impression that it is over half kaolinite. Clay is not dominantly or essentially kaolinite in that sense.

Petrographic Applications

Geologists are frequently called upon to correlate the origin and the mineral nature of clay beds. In estimating the minerals of shale in the absence of all data, the calculation of Leith and Mead (Table XV) is the best guide. In case the field occurrence is known or a sample is available, the estimate may be much improved. Residual clays, glacial clays and loess, and water laid clays have each some mineralogical peculiarities.[2] The physical properties may be tested with additional evidence of minerals. Finally, the presence of certain minerals in the coarser fractions may be combined with the tendencies shown in Table XV to make the best estimate now possible, short of a calculation from analysis.

Relation of Fluxes to Fusibility

It has long been understood that in general an increase in the amount of certain impurities in kaolinite makes it less refractory. Attempts have been made to assign definite fluxing power to oxides of iron, magnesium, calcium, sodium and potassium, found by chemical analysis.[1] Several formulas for estimating refractoriness have been proposed.[2] It is not intended here to extend that work or propose any new formula, but simply to call attention to the nature of the clays that seem to show a fusibility different from that which would be expected from the amount of fluxes present.

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[1] Purdy, *op. cit.*, pp. 203–204.

[2] Summarized by Clarke in U. S. Geol. Surv., *Bull.* **695**, pp. 499–510.

TABLE XVI

	The distribution of fluxes of the whole clays through the several fractions					Comparison of total fluxes and temperatures of viscosity	
	In coarse sand, per cent	In fine sand, per cent	In silt, per cent	In coarse clay, per cent	In fine clay, per cent	Total fluxes, per cent	Temperature of viscosity, °F
1	4.0	3.0	9.5	3.0	1.5	21	2174
2	0.5	0.4	2.2	1.0	2.0	6	2426
3	0.2	0.2	8.0	2.4	7.5	18	2174
4	0.4	2.0	6.3	0.2	0.2	9	2166
5	3.9	4.4	4.7	0.2	trace	14	2345
6	0.7	0.3	8.0	4.4	2.5	18	2166
7	trace	trace	7.0	5.7	6.2	19	2102
8	trace	trace	18.8	2.3	2.0	23	2174
9	trace	0.1	8.3	1.2	1.0	11	2210
10	trace	trace	13.4	4.0	2.0	20	2138
11	0.6	3.4	15.9	0.5	0.2	19	2066
12	1.0	4.6	11.4	1.2	1.3	20	2174

Relation of Fineness to Fusibility

The diagram (Fig. 2) shows the relation between the amount of fluxes in these Minnesota clays and the temperature of viscous fusion. Of the twelve clays tested, two fall notably below the curve and two are high above.

The two clays, No. 5 and No. 8, with exceptionally high temperatures of viscosity, have their fluxes mostly in the sand and silt. Clay No. 1 has a tendency the same way.

On the contrary, clays No. 4, 7, 9, and 11 fuse at lower temperatures than average. Clay No. 7 has its fluxes in the fine portions where they might be expected to exert their full influence at low temperatures. Clays No. 4 and 11, however, seem to have no such abundance of fine fluxing matter. By reference to the tables, however, it will be seen that although the clay fraction is small in amount it has a composition high in fluxes. In other words, although these two samples have very little clay of the finest sizes, that small portion is very fusible.

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[1] Richter's laws published in 1868, critically reviewed by Cramer in 1895, are valuable. See E. Cramer, *Tonindustrie Zeit.* (1895). Curves are given by R. C. Purdy in Ill. Geol. Surv., *Bull.* **9**, 207–210 (1908).

[2] H. A. Wheeler, "Clay Deposits," Mo. Geol. Surv., **11**, 143–153 (1896).

This raises the question whether the temperature of viscosity is most influenced by the *amount* of fine flux or by the *fusibility* of a small amount of fine flux.

Figure 1 is drawn to show the relation of temperatures of viscosity to the per cent of fluxes in the finest fraction of the clay. If this is compared with Fig. 2, it is easily seen that the several samples fall closer to the curve than the same samples plotted by the method of Fig. 2. This strongly confirms the suggestion that *the nature of the fine clay is of more influence than its amount,* so long as it constitutes a few per cent of the whole.

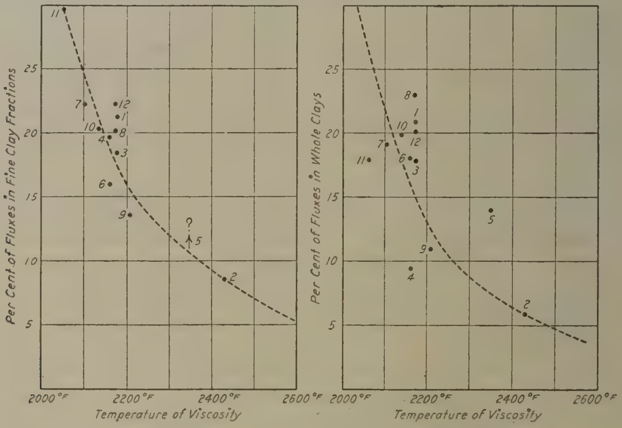

FIG. 1. FIG. 2.

FIGS. 1 AND 2.—Curves of the relation between fluxes in clays and their temperatures of viscous fusion. Note first that the fusion points seem to be more uniformly close to the curve when plotted in relation to the per cent of fluxes in the finest fraction, (Fig. 1) than when in relation to the total fluxes of the whole clay (Fig. 2). Note further that in Fig. 2, clays falling above the curve, No. 1, 5, and 8, have fluxes mostly in the coarser fractions; while those below the curve, No. 4, 7, and 11, have little of their fluxes in the sand, Table XVI.

So far as the writer is aware, none of the formulas proposed for calculating fusibility take into account these two factors; the distribution of fluxes with size of grain, and the per cent of fluxes in the finest size. Since each has probably a definite effect, the formulas are necessarily inaccurate; but no accurate formula can be proposed without such an elaborate study that the fusibility can be much more readily determined by experiment than by calculation. The futility of attempts to calculate fusion from analysis is shown by a simple list of the factors which are known to modify the result but modify it to a wholly uncertain degree, *viz.* (1.) Average size of grain of the clay. (2.) The mineral combination of the oxides. (3.) The distribution of fluxes through the several sizes. (4.) The per cent of fluxes in the fine clay portion.

It is noteworthy that Wheeler's formula[1] which gives extra weight to alkalies as fluxing ingredients, while not justified by the experimental work of Richter, and of Cramer, may be somewhat justified by the tendency of potash to concentrate in the fine clay fraction as shown in tables above. Potash is doubly active in most clays, because it is not only a flux for the clay as a whole, but is most abundant in the fine clay, the fusibility of which is the most important factor in determining the viscosity of the mass.

Mixing Clays

Analyses of crude clays showing the proportion of fluxes can hardly be a safe guide as to the effect of the clay when used as a binder or admixture for other clays. Referring to Table XVI, clay No. 7 with most of the fluxes in coarse and fine *clay* fractions must certainly yield different results from clay No. 11 or No. 12 where the fluxes in the clay fractions are less than 2%, though all have about the same amount of fluxes in the crude clay.

Here again the dominance of *composition of fine clay* in control of viscosity may be suggested. If the fine clay portion of an added bond is of the correct fusibility, the coarse may be of considerable variety without much effect. This may be of great importance in determining the availability of a clay before more expensive practical tests are made in the kiln.

Beneficiation of Clays by Washing

Clays No. 1 and No. 2 are washed commercially. No. 1, the gray drift, is stirred up with excess of water in a pit. A bucket elevator of

TABLE XVII

CLAY NO. 1 AND ITS COMMERCIALLY WASHED FRACTIONS

		Clay artificially settled after removal of gravel			
	Whole clay	Sand near intake	Sand near center	Clay near center	Clay far from intake
Silica	58.85	70.21	62.60	50.65	50.55
Alumina	7.25	6.27	6.96	9.01	9.41
Iron oxides	4.97	3.16	3.75	5.26	6.19
Magnesia	3.45	1.55	3.59	3.60	3.62
Lime	9.42	7.28	7.78	10.20	10.20
Soda	1.37	2.11	1.94	1.32	1.22
Potash	1.76	1.53	1.82	1.83	1.85
Ignition	2.10	1.38	2.90	6.10	6.05
Moisture	2.10	.60	1.80	3.40	3.10
Titania	.36	.19	.33	.53	.60
Carbon dioxide	9.10	6.00	7.10	8.20	8.00
	100.73	100.28	100.57	100.10	100.79

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[1] *Op. cit.*

continuous operation dips into the pit near the center, and removes the gravel. At the side of the pit a screen allows the sand and clay to escape into settling ponds, where some of the water can be pumped off and some settles into the ground. The sand settles mostly near the intake and the clay is carried to the farther side. The samples from several parts of such an artificial deposit show general concordance with the laboratory washing.

Clay No. 2 is a stoneware clay washed commercially by a very different process. The crude clay is reduced to a slush and the sand removed in rotary sieves (80-mesh), after which the clay goes to large filter presses. The commercial separation yields a purified product resembling a mixture of the silt and clay portions of the mechanical analysis. The analyses of the sand of the laboratory separation and the refuse of the commercial washing agree perfectly in showing that the improvement results from a removal of iron oxide concretions and quartz.

TABLE XVIII

CLAY NO. 2 AND ITS COMMERCIALLY SEPARATED FRACTIONS

	Whole clay	Washed clay	Refuse from washing
Silica	69.92	69.26	64.98
Alumina	17.39	18.57	11.38
Iron oxides	1.68	1.93	12.03
Magnesia	1.11	.62	2.51
Lime	.60	.45	.68
Soda	.07	.06	.00
Potash	2.25	2.41	1.93
Ignition	5.45	5.58	5.28
Moisture	1.10	1.10	1.08
Titania	.63	.77	.71
	100.20	100.75	100.58

It may be said without much possibility of question that the improvement in both these clays, and the nature of the improvement, could have been foretold from a laboratory study of the chemistry of the fractions separated in a mechanical analysis. It may easily happen that such a study will save a large investment in experimental washing plants.

STATE GEOLOGIST
MINNEAPOLIS, MINN.

THE DEAD BURNING OF DOLOMITE—II[1]

By James Thomas Robson and James R. Withrow

Preliminary Investigation

There are many large deposits of dolomite in the United States. These range from the very pure dolomite of Ohio and the eastern states, notably New York and Pennsylvania which correspond very closely to the theoretical formula $CaCO_3$ $MgCO_3$ to dolomites which are very low in MgO content.

Throughout this work, a pure variety of dolomite obtained from the Niagara deposit at Cedarville, Ohio, was used.

It analyzed as follows:

Silica (SiO_2)............	0.4	Potassium oxide (K_2O)...	trace
Aluminum oxide (Al_2O_3)..	0.5	Sodium oxide (Na_2O).....	trace
Ferric oxide (Fe_2O_3).....	0.5	Sulfur trioxide (SO_3).....	none
Calcium oxide (CaO)....	30.2	Carbon dioxide (CO_2)....	46.8
Magnesium oxide (MgO).	21.8		
			100.2

The true specific gravity of this dolomite is 2.85.

This dolomite was crushed in jaw crushers, then ground through rolls and finally ground in the dry pan until it all passed 100 mesh, which Schurecht[2] found to be the best degree of fineness. After the entire batch had been screened, it was again thoroughly mixed for about 15 minutes in a dry pan so that the harder material was evenly distributed throughout the softer material which passed through the screen first.

Series 1A

The pulverized dolomite was then mixed with Al_2O_3, Fe_2O_3 and SiO_2 in the proportion of 90% dolomite by weight to 10% of flux by weight maintaining the 90% of dolomite constant and blending the 10% of fluxes in a three variable series consisting of twenty-two members apportioned as follows:

Number	Fe_2O_3	Al_2O_3	SiO_2	Number	Fe_2O_3	Al_2O_3	SiO_2
1A1	10	..	..	12	2	8	..
2	8	2	..	13	2	6	2
3	8	..	2	14	2	4	4
4	6	4	..	15	2	2	6
5	6	2	2	16	2	..	8
6	6	..	4	17	..	10	..
7	4	6	..	18	..	8	2
8	4	4	2	19	..	6	4
9	4	2	4	20	..	4	6
10	4	..	6	21	..	2	8
11	3.33	3.33	3.33	22	..	..	10

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[1] The first paper in this series appeared in *Jour. Amer. Ceram. Soc.*, **7** [1], 61(1924).

[2] *Jour. Amer. Ceram. Soc.*, **4** [2], 133(1921).

J. T. Baker's analyzed alumina and ferric oxide, also flint obtained from the Pennsylvania Pulverizing Co., were used as fluxes. These analyzed as follows:

Alumina		Ferric oxide		Flint	
Al_2O_3	99.99%	Fe_2O_3	99.99%	SiO_2	99.81%
SiO_2	0.001%	FeO	trace	Al_2O_3	0.17%
Fe	.005%	SO_3	0.007%	Fe_2O_3	0.014%
CaO	.001%			CaO	none
Cl	.001%			MgO	none
SO_3	.001%				

These analyses were made on the samples after drying at 105°C. The amount of moisture present in each was as follows:

Alumina	Ferric oxide	Flint	Dolomite
0.24%	0.32%	0.07%	0.11%

Moisture

In all compositions, corrections were made for moisture, *e. g.*, a 3200 gram batch of member 1A calls for 2880 grams of dolomite (=90%) and 320 grams of iron oxide (=10%). The amount of moisture in the dolomite is 0.11%, therefore $\frac{2880}{(100-0.11)} \times 100 = 2883.2$ grams of dolomite required. The moisture in the iron ore is 0.32%, hence $320 \div (100-0.32) \times 100 = 321.03$ grams of iron ore were added to 2883.2 grams of dolomite giving a 90% dolomite and 10% ferric oxide mixture.

The end members 1A1, 1A17 and 1A22 were prepared by grinding the dolomite with the respective oxides in the dry pan for about one hour or until the added flux was thoroughly mixed throughout the dolomite as shown by a very uniform color. These end members were then blended, so as to produce the intermediate members by weighing out the proper quantity of each.

Thoroughly mixing with a spatula, rolling back and forth on paper and screening through a 40-mesh screen twice. After this mixing which required about 20 minutes for each member of 400 grams, the blends were uniform in composition as shown by the uniformity of color in members where iron oxide was used.

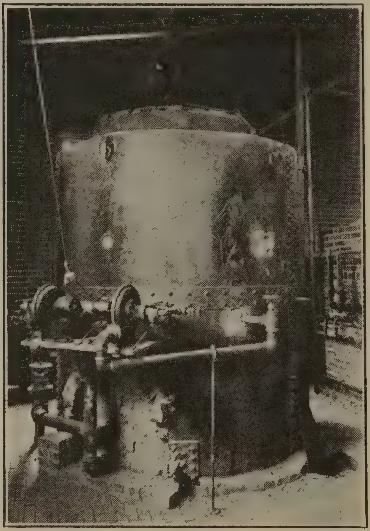

FIG. 11.—Gas fired kiln.

One-inch cubes of the various mixtures were made by tempering the mix with water until it molded well. The average amount of water required was about 20% on the dry weight basis. The dry cubes were burned in a down-draft gas fired furnace shown in Fig. 11, to cone 16 down. The time for the burn was 54 hours. The temperature of burning as recorded by the pyrometer at 2-hour intervals is shown in Fig. 12. The curve is given to show the approximate rate of burning. Cones were placed throughout the kiln and all plaques of cones after the burn showed the heat to be evenly distributed throughout, that is, cone 16 down.

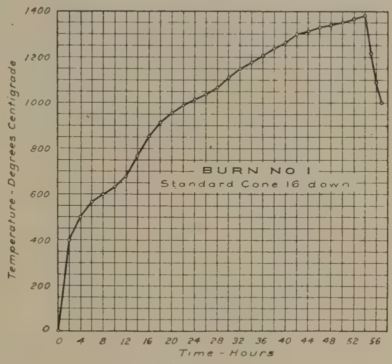

Fig. 12.

Burning Results of Series 1A

The colors of the burned cubes varied from black in the high iron oxide field to light brown in the alumina field to a pale green in the silica field. These colors are to be expected, the black due to the iron, the brown due to the alumina as in Portland cement clinker and the green similar to an ordinary lime silica slag. For colors of each member, see the following (Table I).

Table I

Color of Burned Cubes

Series 1A		Series B	
Member	Color	Member	Color
1–15	Black	1–16	Black
16	Dark brown	17	Brown
17	Light brown	18	Brownish green
18	Greenish brown	19–23	Green
19	Pale green	24	Yellowish green
20–21	Bluish green		
22	Yellowish green		

These cubes were set in the kiln on chrome powder spread over silica brick, to prevent fluxing between the dolomite and silica. Cubes of each member were also placed in the kiln on silica brick alone. Because of their strongly basic action, the cubes in contact with the silica fluxed partially down into the brick. Members 5, 6, 19 and 21 dusted down completely in the kiln when supported on silica brick. This was due to the formation of calcium orthosilicate and its consequent inversion from the beta to the gamma form as previously described in the introduction. This presence of the orthosilicate was confirmed by examination of some of the dust under the microscope. No cubes which were set on powdered chrome completely disintegrated in the kiln; however, there was slight dusting on the bottom of all the cubes when they came in contact with the ore.

After removing the cubes from the kiln, the following properties were tested on separate cubes:

1. Air slaking resistance at room temperature.—Determined by allowing the cubes to stand in the laboratory and noting once per week the time at which they started to disintegrate or dust down.

2. Outside air slaking resistance.—Determined by allowing the cubes to stand outside on the window sill and noting when disintegration started.

3. Hot water test.—Cubes were placed in a pan of water and placed on the hot plate. The temperature of the water varied from 70–80°C. The water was renewed each day. Several times, due to fluctuation in the gas pressure, the water in the pan evaporated over night. In this case, without allowing the pan and its contents to cool, water directly from the faucet was run in on the hot cubes and the pan again placed on the hot plate.

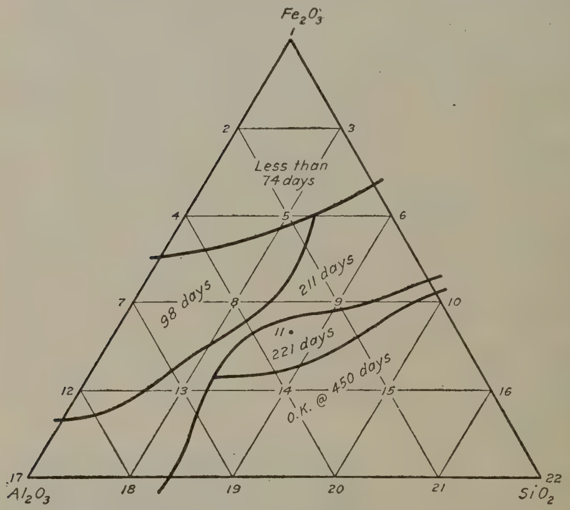

FIG. 13.—Room temperature air slaking test of series 1A.

Results of Tests on Series 1A

Room Temperature Air Slaking Test.—The results of the room temperature air slaking test are given in Table II and shown on Fig. 13. Here it is seen that the mixtures high in iron oxide are the least stable,

TABLE II

SERIES 1A

Air slaking test at room temperature

Cube no.	No. of days exposed before disintegrating	Order of slaking
1–5	71–73	First
7, 8 and 12	98	Second
6, 9, 13, 17 and 18	211	Third
11	221	Fourth
10, 14, 15, 16, 19, 20, 21, 22	Not slaked after 450 days' exposure	Fifth

Outside air slaking test

Cube no.	No. of days exposed before disintegrating	Order of slaking
1, 2 and 4	50	First
3	71	Second
5	92	Third
7, 8 and 12	106	Fourth
13, 17 and 18	149	Fifth
9 and 16	223	Sixth
6, 10, 11, 14, 15, 19, 20, 21, 22	Not slaked after 450 days' exposure	

Hot water slaking test

Cube no.	No. of days soaked before disintegrating	Order of slaking
1, 2, 3, 4, 5, 7, 8, 12 and 17	1	First
13 and 18	2	Second
16, 19, 21 and 22	5	Third
6 and 10	18	Fourth
9, 11, 15 and 20	50	Fifth
14	99	Sixth

whereas coming down toward the silica field, members 14, 15, 16, 19, 20, 21, and 22 have not yet disintegrated after 450 days' exposure, showing them to be very stable at room temperature when protected from the weather, so that it appears as though silica, 10% or less, stabilizes calcined dolomite with regard to slaking in the air.

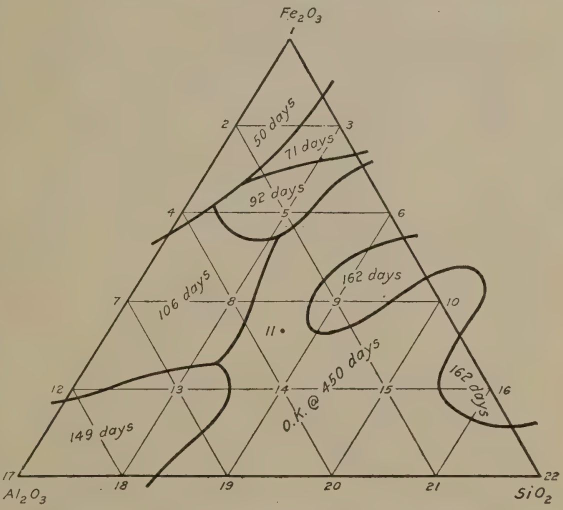

FIG. 14.—Outside air slaking test of series 1A.

Outside Air Slaking Test.—The results of this test shown in Table II and Fig. 14, follow somewhat according to the order of those obtained in the room temperature air slaking test, more accelerated in some cases and slower in others. Here again in general, the high iron region slaked down first, the high alumina region next. The middle region and that of the silica field are the most stable. As shown, these stable compositions have not slaked after 450 days' exposure in the air.

After about two weeks' exposure, all cubes were covered in places with a white coating which upon analysis proved to be $CaCO_3$. This lime was no doubt due to free lime present in the cube combining with CO_2 from the air.

Two cubes of each member were tested here and in all cases those of the same composition disintegrated at the same time.

As mentioned, this test does not appear to be much different from the inside slaking test.

Hot Water Slaking Test.—For results of this test see Table II and Fig. 15. Here again, the region high in iron is the most unstable together with the members highest in alumina. In general, the field high in Al_2O_3 is more unstable than that in the silica field. However, the most stable field appears to be near the middle of the diagram, where all three oxides are present.

By far, the most stable composition in this series is member 1A14, whose composition is as follows:

Dolomite	90.0%
Fe_2O_3	2.0
Al_2O_3	4.0
SiO_2	4.0

This composition gives a formula as follows:

$$\left.\begin{matrix} 0.5\ CaO \\ 0.5\ MgO \end{matrix}\right\} \left.\begin{matrix} 0.0399\ Al_2O_3 \\ .0128\ Fe_2O_3 \end{matrix}\right\} 0.0685\ SiO_2.$$

In fact, this body 1A14 did not actually slake down. It simply cracked into three or four pieces after heating in warm water for 99 days. In the immediate field around 1A14 toward the SiO_2 corner as shown in Fig. 14, members 1A9, 1A11, 1A15 and 1A20 were the next most stable, withstanding this boiling test for 50 days before breaking down. These members like 1A14 simply cracked into 3 or 4 pieces and did not slake down into a powder as was the case with the more unstable compositions. This cracking may have been due to an expansion and contraction effect, since cold water was occasionally poured on the hot cubes as described in the method of procedure. It is

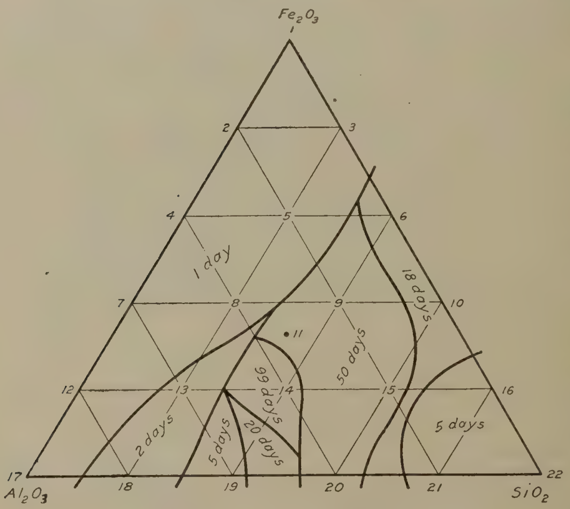

FIG. 15.—Warm water slaking test of series 1A.

thus seen that with this more severe and more accelerated test, the central field again proves to be the most stable, being more stable than the high silica field. In this test a considerable scum of $CaCO_3$ formed on the surface of the water in which the bodies were immersed.

Two cubes of each member were used in this test and again both slaked at the same time.

Series B

The next preliminary study was made in series B consisting of a twenty-four member series blending 90% of dolomite constant with 10% of variable fluxes blended on the molecular basis. The molecular ratios and corresponding percentage compositions by weight for this series are shown in Table III.

TABLE III

			Percentage composition	
Member	Molecular ratio	Fe_2O_3	Al_2O_3	SiO_2
1	Fe_2O_3	10.0	...	...
2	$.8Fe_2O_3\ .2Al_2O_3$	8.625	1.375	...
3	$.8Fe_2O_3\ .2SiO_2$	9.140	...	0.860
4	$.6Fe_2O_3\ .4Al_2O_3$	7.010	2.990	...
5	$.6Fe_2O_3\ .2Al_2O_3\ .2SiO_2$	7.475	1.590	0.935
6	$.6Fe_2O_3\ .4SiO_2$	8.000	...	2.000
7	$.4Fe_2O_3\ .6Al_2O_3$	4.730	5.270	...
8	$.4Fe_2O_3\ .4Al_2O_3\ .2SiO_2$	5.480	3.500	1.020
9	$.4Fe_2O_3\ .2Al\ O_3\ .4SiO_2$	5.900	1.885	2.215
10	$.4Fe_2O_3\ .6SiO_2$	6.400	...	3.600
11	$.33Fe_2O_3\ .33Al_2O_3\ .33SiO_2$	4.965	3.165	1.865
12	$.2Fe_2O_3\ .8Al_2O_3$	2.820	7.180	...
13	$.2Fe_2O_3\ .6Al_2O_3\ .2SiO_2$	3.04	5.82	1.14
14	$.2Fe_2O_3\ .4Al_2O_3\ .4SiO_2$	3.300	4.220	2.480
15	$.2Fe_2O_3\ .2Al_2O_3\ .6SiO_2$	3.620	2.310	4.070
16	$.2Fe_2O_3\ .8SiO_2$	4.000	...	6.000
17	Al_2O_3	...	10.00	...
18	$.8Al_2O_3\ .2SiO_2$	...	8.720	1.280
19	$.6Al_2O_3\ .4SiO_2$	...	7.180	2.820
20	$Al_2O_3\ SiO_2$	...	6.300	3.700
21	$.4Al_2O_3\ .6SiO_2$	...	5.320	4.680
22	$Al_2O_3\ 2SiO_2$	...	4.600	5.400
23	$.2Al_2O_3\ .8SiO_2$	...	2.980	7.020
24	SiO_2	...	...	10.00

Member B20 contains Al_2O_3 and SiO_2 in the proportion in which they exist in sillimanite ($Al_2O_3 \cdot SiO_2$), while member B22 contains Al_2O_3 and SiO_2 in the same proportion as they exist in kaolin. These members were prepared in the same manner as those in series 1A, being made into cubes and burned with series 1A.

The members of this series were all burned on chromite powder. Because of lack of material only 3 cubes of each member were made.

Color

The cubes in general were the same color as in series 1A, *i. e.*, those containing Fe_2O_3 were black, Al_2O_3 gave a pale brown color and SiO_2 gave a green color. For colors of each member see Table I.

Results of Tests on Series B

Inside Air Slaking Test.—But one cube of each member was exposed to this test. The results are given in Table IV and Fig. 16. Here it is seen as likewise in series 1A, the unstable field is again toward that high in iron and the stable field toward the silica end of the diagram. In this series the very unstable iron field includes two more members, B4 and B6, than series 1A. However, the general slaking fields are very close to being the same, the more stable field again, being down toward the high silica region. Eight of the members as shown, are still stable after 450 days' exposure. It is noticeable that members 1A and B series, which have the same or nearly the same percentage composition by weight, also agree very closely in their air slaking resistance. These members are 1A3 and B6; 1A6 and B10; 1A10 and B16; 1A19 and B20. For example, 1A3 containing 8% Fe_2O_3 and 2% SiO_2 and B6 containing the same percentage of oxide both slaked after about 71 days exposure; 1A6 containing 6% Fe_2O_3 and 4% SiO_2 and B10 containing 6.4% Fe_2O_3 and 3.6% SiO_2 slaked after 211 days and 220 days, respectively. 1A10 and B16 having the same composition are still stable after 450 days' exposure. 1A19 containing 6.0% Al_2O_3 and 4.0% SiO_2 and B20 containing 6.3% Al_2O_3 and 3.7% SiO_2 are still stable after 450 days.

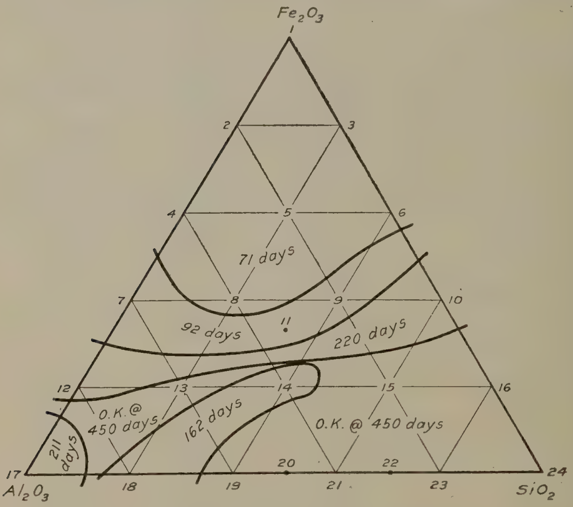

FIG. 16.—Room temperature air slaking test of series B.

Thus it appears that with 10% of flux and 90% of dolomite the percentage composition of the fluxes may be varied slightly among themselves without making any very noticeable change in the air slaking resistance of the calcined mixture.

TABLE IV

SERIES B

Air slaking test at room temperature

Cube no.	No. of days exposed before disintegrating	Order of slaking
1, 2, 3, 4, 5, 6, 8	71	First
7, 9, 11	92	Second
14, 18	162	Third
17	211	Fourth
10, 12	220	Fifth
13, 15, 16, 19, 20, 21, 22, 23, 24	Not slaked after 450 days' exposure	

Hot water slaking test

Cube no.	No. of days soaked before disintegrating	Order of slaking
1, 2, 3, 4, 5, 6, 7, 11, 12	Less than 1	First
8, 9, 10, 14, 17, 19, 20	Less than 2	Second
18, 24	5	Third
16	18	Fourth
13, 22	68	Fifth
15	72	Sixth
21, 23	Not slaked after 99 days	

Hot Water Slaking Test.—The results are given in Table IV and Fig. 17. The region high in iron is the most unstable. The region highest in Al_2O_3 and that near the middle of the three fields are next, while the most stable members are B21 and B23 whose flux molecular ratios are $.4Al_2O_3.6SiO_2$ and $.2Al_2O_3.8SiO_2$ respectively, neither contains any Fe_2O_3. These two members after undergoing the boiling test for 99 days without slaking or cracking were allowed to stand in the air at room temperature for 172 days, then placed in the hot water bath described later and broke down after soaking four days in water at a temperature of 75–85°C.

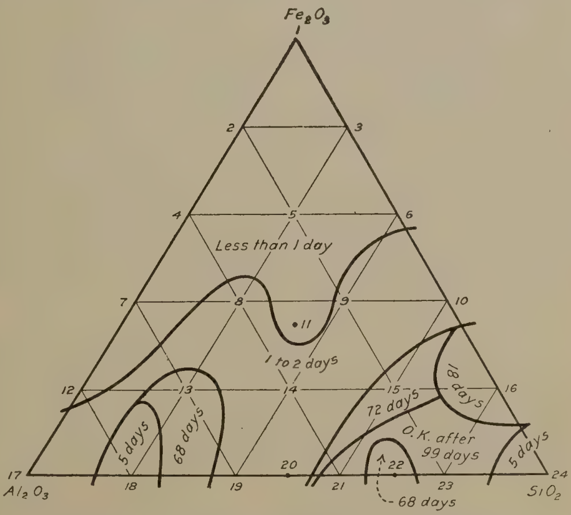

FIG. 17.—Warm water slaking test of series B.

Contrary to the air slaking test, a slight variation in the percentage composition of the fluxes appears to affect the water slaking resistance of the cubes quite noticeably, *e. g.*, 1A6 which contains 6% Fe_2O_3 and 4% SiO_2 and B10 which contains 6.4% Fe_2O_3 and 3.6% SiO_2 slaked after 18 days and 2 days respectively. 1A19 (6% Al_2O_3 and 4% SiO_2) and B20 (6.3% Al_2O_3 and 3.7% SiO_2) slaked after 5 days and 2 days respectively which tends to show that a slight variation in the ratio of Fe_2O_3 to SiO_2 has more effect on slaking properties of these mixtures than slight variations in the ratio of Al_2O_3 to SiO_2. It is also true that slight variations in the ratio of Fe_2O_3 to Al_2O_3 have a more decided effect than variations of Al_2O_3 to SiO_2. This is due to the fact as shown by the diagram, Fig. 16, that Fe_2O_3 is the least efficient of the fluxes in producing dead-burned dolomite under these conditions.

No outside air slaking test was run on Series B because of lack of material.

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ORIGINAL PAPERS

A STUDY OF PLASTICITY BY PRACTICAL POTTER'S METHODS[1]

BY PAUL E. COX

ABSTRACT

By the use of the potter's wheel it is shown that bentonite added to non-plastic and lean ceramic materials will produce plasticity of the same quality as that found in high grade ball clays. Curves show the results obtained. The colloid theory of plasticity is sustained and it is demonstrated that mineral colloids of the type of the bentonites are of great value in ceramic work where plasticity is highly important.

Introduction

The colloid theory of plasticity has been generally accepted as correct. The object of the work described has been to develop plasticity in non-plastic and short mineral mixtures by the addition of the colloidal mineral bentonite.

Method of Experimental Work

All proportioning of mineral materials was done by dry weight. The first series of experiments was run on mixtures of calcined Florida clay and bentonite, while the second series of experiments was run on North Carolina kaolin and bentonite.

The mixtures of calcined Florida clay and bentonite were wet ground in a ball mill until they would pass a 100-mesh sieve, then dried on plaster until stiff enough to work on the potter's wheel. The mixtures of North Carolina kaolin and bentonite were covered with water, slaked, and lawned

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[1] Presented at the Atlantic City Meeting, February, 1924.

through a 60-mesh sieve and dried on plaster until stiff enough to work on the potter's wheel. Vases were made from all the mixtures that were plastic enough to permit of this process. As a standard of plasticity under this method, Kentucky ball clay was used. The Kentucky ball clay was drawn into as thin-walled a vase as was possible and the other samples were made to match this vase as nearly as possible. All pieces so made were burned at cone 02 in a small commercial kiln.

Wheel Technique Used

The methods followed by the stoneware turner were used in forming the vases. A stoneware potter working on the wheel is known as a turner and does not manipulate his clay as does the whiteware thrower. The ball is centered without forcing the clay to rise into a slender cone which is then forced down again, as is the custom of the whiteware thrower. The ball is then opened either with the fingers or the ball opener. Short clays will split in vertical cracks under this process.[1] All mixtures were rejected as non-plastic which split in opening or which would not yield wares which would be commercially possible of production, under the conditions of the experiments.

Results

Results are shown plotted with the percentages of bentonite on the abscissas and the ease of forming or plasticity on the ordinates. The calcined Florida clay was sensibly coarser than the North Carolina kaolin, which explains the difference in the curves. The plasticity percentage had, of course, to be estimated.

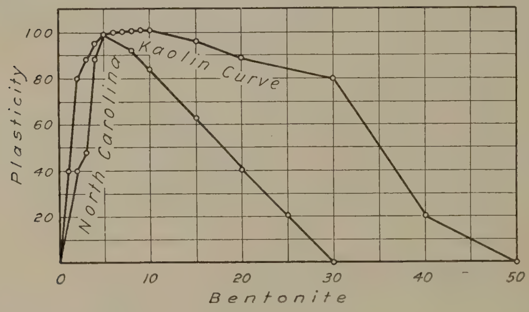

FIG. 1.

Conclusions

1. Bentonite has no plasticity under the conditions of the experiment.

2. Wet ground calcined clay has no plasticity under the conditions of the experiment.

3. Bentonite added to some mineral mixtures will produce plasticity. This plasticity is the exact plasticity found in clays liked by the practical potter.

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[1] Many experiments have proved that clays which behave well on the potter's wheel will behave accordingly on brick and tile machines.

4. North Carolina kaolin mixed with bentonite can be made to have all the plasticity of a high grade ball clay.

5. If a bentonite or similar mineral can be found that is sufficiently free from iron to yield a white burning product, whiteware can be as easily formed as wares made from Number 2 fire clays and the shales of the very plastic sort. There would need to be no more short bodies.

6. It is evident that the finer the grain of the treated mineral the more of the colloidal mineral will be required to effect plasticity. Surface factors are therefore important.

7. It was found that the fusion points of the minerals tested were lowered by the addition of the bentonite. Since very little bentonite causes great increases in plasticity in the coarser grained minerals, this lowering of fusion point can be controlled, when desired.

8. The colloid theory of plasticity has great value in the synthesis of plastic ceramic mixtures.

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A SIMPLE BRICK POROSIMETER[1]

By E. E. Pressler[2]

ABSTRACT

A brick porosimeter based upon the air-expansion principle is described, and various considerations of design discussed. The apparatus described is adapted for testing refractory brick, but the considerations of design presented are general in character. The design is adapted for commercial control work, and the descriptions serve as complete construction references.

Porosity values obtained by the porosimeter and water absorption methods are compared to the values calculated from true sp. gr., to indicate the relative accuracy of the methods.

Introduction

The air-expansion principle for determining open pore space of brick was suggested by Washburn and Bunting.[3] A practical application of the principle in a brick porosimeter was made by Bole and Jackson.[4] The design herein described is developed from this apparatus.

The primary object has been to perfect a porosimeter suitable for rapid routine control testing. A simple and rigid construction, in which refinements for accuracy are under control, is therefore employed.

The Apparatus

The assembled apparatus is shown in Fig. 1. The brick container is made of $^1/_4$-inch rolled boiler plate steel, with inside dimensions slightly larger than the standard dimensions of refractory brick. A cover plate, of the same material, is fixed with 8 wing nut bolts and made air tight by a rubber gasket $^1/_{32}$-inch thick. A simple open-end manometer is connected directly with the brick container. A Cenco-Nelson vacuum pump driven by $^1/_8$-h. p. motor, exhausts the air from the container. A one-liter acid bottle is used as an auxiliary air container. To the air inlet tube is connected an air-drying attachment, which will be discussed later more fully.

Procedure of Testing

A dry brick is placed in the container, the gasket seal is rendered air-

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[1] The writer wishes to express his appreciation for many helpful suggestions and criticisms received from G. A. Bole and F. G. Jackson of the Ceramic Station of the U. S. Bureau of Mines, Columbus, Ohio and R. C. Purdy, General Secretary of the American Ceramic Society.

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[2] Ceramic Assistant, U. S. Bureau of Mines, Ohio State University, Columbus, Ohio.

[3] "Porosity VII. The Detn. of Porosity of Highly Vitrified Bodies," *Jour. Amer. Ceram. Soc.*, **5** [8], 535–37 (1922).

[4] "A Simple Control Porosimeter," *Brick & Clay Rec.*, **61** [5], 314–15 (1922).

tight by a light application of vacuum wax, and the cover plate bolted down securely. The desired degree of vacuum is created in the brick container, while the auxiliary air container is adjusted to atmospheric pressure. The manometer is read when connected with the brick container alone, and again when the two containers are connected. Several check readings are usually taken. The brick is then removed and its volume determined by calipers, if of regular shape, and if not, by water displacement.

The Containers

Washburn and Bunting[1] pointed out that the first partial vacuum may be induced in either the test piece container or the auxiliary air container. If the pump is connected directly to the test piece container, a smaller auxiliary air volume will suffice to give the desired manometer scale range. The direct connection is preferred for the further reason that the suction of the pump may then be used to remove from the system any adsorbed gas or liquid in the brick, which volatilizes at the reduced pressure.

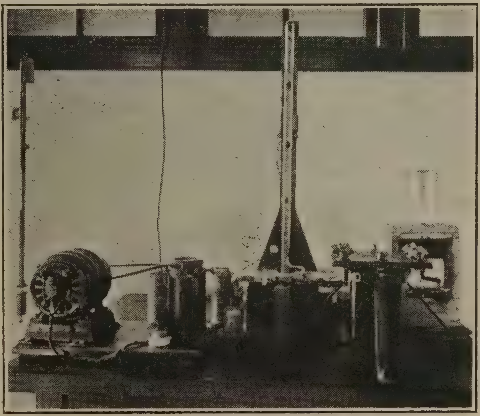

FIG. 1.

The gasket and bolted cover plate method of closure is found to be more effective than a glass plate ground in place. Practical tests indicate that the application of pressure is necessary to prevent leakage under high pressure-differences.

To secure the desired rigidity, the brick container is set into a fixed position on the supporting base, and firmly fastened by means of an iron collar and legs.

Relative Size of Containers

It is desired to keep total volumes small so that manometer readings may be as sensitive as possible. To allow for irregularities in the shape and size of bricks to be tested, the brick container is designed with a tolerance of $^1/_4$-inch in each dimension above the standard size of refractory brick. When an average brick is enclosed, the free air space plus the open pore space are from 700 to 900 cubic centimeters. If an auxiliary air container of approximately equal capacity is used, the maximum range of manometer scale may be utilized without introducing relations of pressure and volume which tend to make calculations inexact.

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[1] "Porosity VI. Determination of Porosity by the Method of Gas Expansion," *Jour. Amer. Ceram. Soc.*, **5** [2], 115 (1922).

The Manometer

Certain advantages in the use of an inclined scale manometer are pointed out by Bole and Jackson,[1] but this refinement complicates construction and calculations and therefore is not used in this design. A vertical open end manometer is preferred to a closed end manometer or simple barometer, for convenience in taking readings. It requires the observation of only one mercury column level, since the other is kept stationary, whereas the sealed end type requires observation of both mercury column levels.

A manometer tube of the least cross-section which will allow free movement of mercury is desirable, from considerations of accuracy and design. A glass tube with a bore of about 2.7 millimeters is used, but it does not permit ready adjustment to pressure changes without vigorous tapping. A slightly larger bore would be preferable for this reason, but even then, tapping should not be neglected. For tapping the tube, an electric doorbell may be adapted.

The surface area of the mercury in the pan is such that the varying height of the mercury column will not cause a significant variation in the level of mercury in the pan. The minimum allowable mercury surface is calculated from the ratios:

$$\frac{\text{area of manometer section}}{\text{area of mercury surface in pan}} = \frac{\text{max. variation in pan level}}{\text{av. depr. of mercury column}}$$

With a manometer tube bore of 0.055 square centimeter, an average mercury column depression of 40 centimeters, and a maximum variation in pan mercury level of 0.01 centimeter, the minimum area of pan mercury surface, $X = \frac{.055 \times 40}{0.01} = 220$ square centimeters. A 6 x 8-inch hard rubber photographer's washing tray is convenient for this purpose.

The mercury pan is set in a wooden frame about 6 inches above the general table level. The manometer tube is attached to a meter stick, and fixed by screws and cork washers to an upright standard extending from the mercury pan support. The manometer tube should extend at least 76 centimeters above the lower mercury surface.

Calibration

The volume of each container together with its immediate connections, is determined directly by weighing when empty and filled with distilled water. The true volumes are obtained by dividing the observed volumes by the relative density of water at the temperature of weighing. The volumes of the various connections and the manometer tube bore are found by determining the weight of mercury required to fill them, and dividing by the specific gravity of mercury.

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[1] Bole and Jackson, *loc. cit.*

The volume of the connections included with the brick container, and the section of manometer tube bore up to the mercury column height for the first reading, are included as a part of the brick container. The volume of manometer tube bore added to the system incident to connecting the auxiliary air container is computed, and this is considered as an integral part of the volume of the air container. Using the values thus obtained, the volumes of the empty containers are checked against each other by test trials.

Method of Calculation

Let V_1 = corrected volume of brick container
V_2 = corrected volume of auxiliary air container
R_1 = first reading of mercury column
R_2 = second reading of mercury column
P_1 = pressure indicated by R_1
P_2 = pressure indicated by R_2
P_B = barometric pressure
V_B = bulk volume of brick
P = per cent porosity
V_1^1 = total air space in brick container with a brick inserted, including the open pore space of the test brick.

Assuming constant temperature and barometric pressure, the relations with a brick in place are:

$$V_1^1P_1 + V_2P_B = (V_1^1 + V_2)P_2 \tag{1}$$

Since actual pressures are measured by differences in mercury column levels,

$$P_1 = P_B - R_1$$
$$P_2 = P_B - R_2$$

Substituting in (1):

$$V_1^1(P_B - R_1) + V_2P_B = V_1^1P_B - V_1^1R_2 + V_2P_B - V_2R_2 \tag{2}$$

Canceling and collecting,[1]

$$V_1^1 = \frac{V_2R_2}{R_1 - R_2}$$

Hence:

$$V_1 - V_1^1 = \text{skeleton volume of brick}$$
$$V_B - (V_1 - V_1^1) = \text{open pore space of brick}$$

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[1] It will be observed that barometric pressure is eliminated from the equation by cancellation, hence the use of actual barometric readings is not required.

$$P = \frac{V_B - (V_1 - V_1^1)}{V_B} \times 100^1 \qquad (3)$$

Sources of Error

1. **Leakage.**—The containers and their connections must be air tight. Before mounting, they are tested separately by filling with air under pressure and immersing in water. The assembled apparatus will indicate leakage by a steady fall of the mercury column when the air is partially evacuated.

All tube connections are made with heavy rubber pressure tubing and are sealed with red lead paste, bound with a double loop of wire belt lacing, and coated with shellac.

2. **Manometer.**—The manometer scale is graduated in millimeters but readings are estimated to 0.1 millimeter. The effect of 0.1 millimeter error in observation, when testing an average brick, was found to be 0.20 cubic centimeter for R_1, and 0.44 for R_2. Consecutive tests of pore space usually agree within 1 cubic centimeter, which indicates that readings may be taken within limits of significant error.

Inspection of formula (2) shows that $V_1^1R_2$ and V_2R_2 become indefinite when R_2 approaches zero. For this reason, readings near zero on the manometer scale are avoided.

The mercury column in the manometer usually comes to a constant level in less than 60 seconds, but in some cases a longer time is required. The causes of such variation have not been definitely ascertained, but apparently depend upon the type of brick tested, or the nature of the brick structure.

3. **Thickness of Rubber Gasket.**—A slight error may be caused by differences in pressures applied in adjusting the gasket and by variations in thickness incident to usage. Careful observations from time to time show this error to be inappreciable, when gaskets are changed frequently.

4. **Moisture.**—Washburn and Footitt[2] noted that exact results require freedom from adsorbed moisture in the test piece. Tests made by them indicate that this is not practically attainable, but that the volume of water content is insignificant when the test piece is carefully dried. Under atmospheric conditions, however, it was shown that an appreciable volume of pore space might be occupied by adsorbed moisture.

Another source of moisture is from the air of the auxiliary air container. To study its effect, a train of absorption tubes of sulphuric acid and calcium

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[1] This corresponds to the formula, $P = \frac{W - D}{W - S} \times 100$, which was derived by Purdy and presented in *Trans. Amer. Ceram. Soc.*, **9**, 211 (1907).

[2] "Porosity III. Water as an Absorption Liquid," *Jour. Amer. Ceram. Soc.*, **4** [12], 965–69 (1921).

chloride was attached to the air inlet tube. The pore volume indicated was about 5 cubic centimeters lower with air thus dried.

The lower values due to moisture occupying pore space in the test piece tend to offset the higher values due to moisture from the auxiliary air. Experimental tests indicate that sufficiently accurate results for most purposes are obtainable with both the test brick and the auxiliary air under atmospheric conditions. For refined work, both the test piece and the auxiliary air should be dried.

5. Temperature and Pressure Effects.—The atmospheric temperature and pressure should be constant between readings, and the test brick and the containers should be in temperature equilibrium. The error effected by a difference of 1°C between containers at 20°C is $\frac{1}{273 + 20} \times 1000$, or 3.4 cubic centimeters. It is important, therefore, that the room in which the porosimeter is used, be not subject to temperature fluctuations, and that the bricks tested be at the temperature of the room.

Comparative Tests

Below are given the results of comparative tests of porosity and specific gravity upon two series of brick, which indicate the efficiency of the porosimeter method of determining porosity.

TABLE I

HEAT TREATMENT	PER CENT POROSITY			SPECIFIC GRAVITY		
				Calculated from porosity		
	Water absorption	Porosimeter	Calculated from true sp. gr.	Water absorption	Porosimeter	True
Series 1						
Silica brick						
Soft-burned	23.67	25.37	25.40	2.394	2.444	2.445
Medium-burned	23.29	26.20	26.26	2.264	2.363	2.365
Hard-burned	24.90	26.80	26.82	2.292	2.321	2.321
Series 2						
Fire clay brick						
Soft-burned	21.91	22.84	22.84	2.667	2.694	2.694
Medium-burned	20.50	21.19	21.44	2.635	2.653	2.661
Hard-burned	12.61	15.68	16.00	2.564	2.651	2.661

A full report on the results of comparative tests on different types of refractory brick will appear in a subsequent issue of this *Journal.*

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BACTERIAL GROWTH IN ENAMEL SLIP[1]

By Joel G. Wahlin

Introduction

While engaged upon some chemical research relative to the manufacture of enamel, R. D. Cooke[2] observed the production of gas in enamel slip water. This was brought to the attention of E. W. Tillotson,[3] and was referred by him for solution to N. P. Sherwood.[4] After carrying out a few preliminary experiments he turned the biological aspects of the problem over to me for investigation.

Cooke observed that the production of gas in enamel slip water proceeded differently in the presence of various ions of the iron family, being most rapid with aluminum—iron, cobalt and nickel being next in order. He also observed that no reaction occurred in the absence of nitrates and acetates. These reactions took place at room temperature and the general nature of the phenomenon, its inhibition by heat, mercuric ion, and formaldehyde, was suggestive of bacterial action, which indeed it has proved to be.

The source of the microörganisms occurring in enamel slip is undoubtedly the clay used. This is indicated by the chemical composition of the enamel slip and the manner of its preparation. No living organisms could survive the temperature to which the enamel frit is subjected (2200°F) and it is therefore reasonable to suppose that contamination occurs upon the addition of clay. Moreover, enamel slip is at best a very poor culture medium for the growth of most bacteria and those that would occur there would of necessity be of an autotrophic nature in certain of their food requirements. Autotrophic bacteria are widely distributed in nature and their presence in clay could be accounted for by percolation of soil water. Owing to a lack of time no attempt has been made to isolate any organisms from clay and to see if such organisms would resemble those found in enamel slip. Such an investigation would not have fallen within the scope of the work as originally planned and has therefore been postponed for future study.

Assuming then that bacteria are carried into the enamel slip with the clay, what characteristics might one expect such organisms to possess? A consideration of the chemical and physical properties of clay might furnish a clue in answer to this question.

The bacteriology of clay is as yet largely an unsolved problem. The reason for this is that agriculturally clay is an unproductive soil and there has been no immediate need for a knowledge of the bacteria present. The rôle of bacteria in clay, from the standpoint of its application to the arts and industries, has not been touched upon to any extent. The physical and chemical composition of clay renders it unsuitable as a culture medium for the growth and development of many bacteria, a property which might be spoken of as a "selective action."

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[1] Portion of a thesis presented to the University of Kansas in partial fulfilment of the requirements for the degree of Master of Arts. Presented at the Atlantic City Meeting, February, 1924. (Enamel Division.)

[2] Mellon Institute and the Columbian Enameling and Stamping Company.

[3] Assistant director of Mellon Institute.

[4] Head of the Department of Bacteriology of the University of Kansas.

Among the chemical compounds occurring in clay, those most commonly met and which would be of importance to the living cell are: aluminum silicate, calcium carbonate, iron oxides, iron sulphides, phosphates, sulphates and the organic matter and nitrogen compounds. Clay is relatively poor in organic matter and the nitrogen occurring in it would probably be associated with the organic material or gain entrance by infiltration from the surface soil.

The substance of the clay is in a state of fine division generally, although there is a great variation in the size of the particles. Around the clay particles or filling the spaces between them is water and this water holds in solution those compounds utilized by bacteria. The paucity of nitrogenous and organic matter would be a factor in limiting bacterial types.

Discussion and Summary

Many denitrifying bacteria have been described in bacteriological literature. With respect to carbon such forms are mostly of the heterotrophic type, in that they require organic carbon for energy purposes. The denitrifier present in enamel slip is no exception to this rule but is characteristic in its inability to utilize carbohydrate. One would not expect to find carbohydrate substances in clay or enamel slip and consequently the organisms present would have to be able to utilize other organic substances. In this case organic salts of certain types seem to serve the purpose.

The nitrate destruction by this organism seems to proceed in two stages. (1) Reduction of nitrate to nitrite. (2) Reduction of nitrite to a gaseous nitrogen. As pointed out before, the presence of peptone seems to favor the reduction of nitrite to ammonia. There may, however, exist the possibility that under these circumstances the ammonia appearing in the culture may be the result of the deaminization of amino acids, since the gas can also be formed in such media. The reduction of nitrate is probably the method of obtaining the necessary oxygen with which to oxidize the carbon. This view is supported by the fact, that under anaerobic conditions nitrate reduction is accelerated. The ability to grow in the absence of air would naturally be of advantage to the cell under anaerobic conditions in clay. In common with many bacteria it shares the ability to grow at lower temperatures. The original sample of slip from which these organisms were isolated, after standing at icebox temperature for a year and a half, contains the organisms in seemingly undiminished numbers.

The rôle of aluminum is not clearly defined. Cooke found that this element favored gas formation. It is probable that repeated cultivation of the organism away from this element, would tend to reduce its sensibility to it. Later work along these lines seems to indicate that manganese has a beneficial effect in this respect. The work done so far, however, points toward the fact that these substances are accessory rather than essential for growth and denitrification.

No symbiotic relationship was found between the pigmented organism and the denitrifier. A mixed culture did not augment growth and gasification. Moreover, the physiological reactions of the two organisms are so nearly parallel that no hint was given as to the possible mechanism of such a symbiosis.

As mentioned earlier in this paper clay and enamel slip by the very natures of themselves would tend to exert a "selective action" on types of bacteria. Such a "selective action" would account for the presence of only two species of bacteria in the sample analyzed and would also account for the relatively "simple" physiological behavior and food requirements of the microörganisms isolated.

A search through bacteriological literature on the classification of microorganisms has failed to reveal any organism identical with those described in this paper. Owing to the fact that the classification of soil bacteria is as yet in a rather unorganized state, I would hesitate to state that these organisms have not previously been described. Just what their position may prove to be in the great group of soil organisms is impossible to state at the present time.

Conclusions

We can conclude therefore that:

1. Enamel slip is not sterile, as evinced by the isolation of two different microörganisms from a sample.
2. One of these organisms is capable of producing gas in the enamel slip by decomposing nitrates present.
3. A strong alkaline reaction is necessary for growth and denitrification by the organism.
4. Metallic ions exert an influence on the rate of denitrification, but are accessory rather than indispensable to the process as well as growth of the cell.
5. There is no symbiotic relationship between the two organisms studied.

I wish to acknowledge my indebtedness to Professor Sherwood for his council and help throughout the work and to Mr. Cooke for the chemical data which led up to this work and his kindness in furnishing the samples of enamel slip.

LAWRENCE, KANSAS

THE OXIDATION OF CERAMIC WARES DURING FIRING.—I. SOME REACTIONS OF A WELL KNOWN FIRE CLAY[1]

By George A. Bole[2] and Frederick G. Jackson[3]

ABSTRACT

After a review of the literature, a chemical laboratory study is made of the gases evolved on heating a lower Kittanning fire clay at various rates to various temperatures in a current of pure oxygen. The rates of evolution of CO_2, SO_2, and SO_3 are determined under varying conditions. Determinations of the remaining sulphur in the clay after heating are made. Possibilities as to the chemical mechanism of sulphur evolution are suggested. Plans for continuation of the work are outlined.

Introduction

The purpose of this investigation[4] is an endeavor to compile fundamental data that may ultimately lead to a clarification of the several special problems that have presented themselves during the industrial kiln investigations which have been carried out by the Bureau of Mines under supervision of the Joint Research Committee of the Four Heavy Clay Products Associations.

The work will first be carried out in a laboratory way, after which commercial conditions will be investigated.

The first phase of the investigation will be a study of the three fundamental variables which govern the oxidation of ceramic bodies, namely: time, temperature, and atmosphere. The bathing atmosphere is to be varied from pure oxygen to pure nitrogen. Carbon dioxide, hydrogen, and methane will also be introduced in some cases.

With this fundamental data in hand, it is hoped to start the investigation of some of the special problems which confront the ceramist during the firing of ceramic ware.

Previous Work

H. A. Seger laid the foundation of the study of these problems. He conducted interesting qualitative experiments on the effect of oxidizing and reducing gases,[5] both with and without an admixture of sulphur-bearing gases on the color of four familiar types of clays, when fired to various temperatures. He also[6] made a thorough quantitative study of the ratio of carbon, hydrogen, oxygen, and nitrogen in the gases of various kilns at all stages of the burn. He pays little attention to sulphur in the clay throughout his work. He states, however, that sulphurous gases passing through a kiln will combine with calcium carbonate to form calcium sulphate and thus prevent the iron from forming a yellow colored ferrous-calcium silicate. The iron is thus left, uncombined with silica, to oxidize. The ferric oxide colors though were a darker, more reddish color. According to him, magnesia and probably alumina act like calcium carbonate in this respect. Throughout his writings, he returns frequently to this subject and produces several comparative analyses[1] in support of this theory. As his data accumulates, he speaks[2] definitely of "a silicate consisting of iron oxide, alumina, lime and silica." He mentions[3] among occasional sources of efflorescence on brick, the salts of iron, chromium, and vanadium.

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[1] Published with the permission of the Director of the U. S. Bureau of Mines.

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[4] This paper is the first of a series on "The Oxidation of Ceramic Wares during Firing."

[5] "Collected Writings," 1, p. 106.

[6] *Ibid.*, 1, p. 135.

At the second meeting of the AMERICAN CERAMIC SOCIETY, W. H. Zimmer[4] stated that water steam is strongly oxidizing. It may convert the sulphur in kiln gases to H_2SO_4, this will convert lime to $CaSO_4$, which will persist to high temperatures.

Edward Orton, Jr.,[5] explained "black core" in brick as due to ferrous iron formed by the reducing action of organic matter. The same statement appeared in *Tonindustrie Zeitung*[6] for the same year. Hopwood and Jackson[7] quote this paper and state that this is due principally to carbonaceous matter in the clay, which, by reason of an insufficient air supply, has been given no opportunity for oxidation; but that the effect of this agent is modified by ferrous oxide, ferroso-ferric oxide, and occasionally by sulphide of iron.

G. C. Matson produced evidence[8] to the effect that black color is due to FeO without carbon being necessarily present.

Hopwood[9] notes that ferric oxide can be changed to the magnetic oxide by prolonged ignition at white heat, but does not believe that this happens in kiln practice. He found no magnetic oxide in tiles heated under oxidizing conditions to 1350°C. In the discussion of this paper, Dr. Jackson stated that he thought that bloating at complete vitreousness was probably due to the formation of a ferrous silicate from ferric and siliceous fluxes. "Was it possible," he said, "that the blisters which form at the same time are due to the evolution of oxygen as the ferric passes into the ferrous on combination with the silicates?"[10]

[1] "Collected Writings," **1,** pp. 354, 355.

[2] *Ibid.,* **1,** p. 374.

[3] *Ibid.,* **1,** p. 382.

[4] *Trans. Amer. Ceram. Soc.,* **2,** 34 (1900).

[5] *Ibid.,* **5,** 407 (1903).

[6] *Tonind. Zeit.,* **1,** 432 (1903).

[7] *Trans. North Staffordshire Ceram. Soc.,* **2,** 100 (1902–3).

[8] *Clay Worker,* **42,** 44(1904).

[9] *Trans. Ceram. Soc.* (English), **3,** 37 (1903–4).

[10] Recent work would point to the greater likelihood of the blisters being due to decomposition of $CaSO_4$ with the evolution of SO_3.

Edward Orton, Jr., and his co-workers have developed the theory now held most generally. Beginning with a hint[1] as to the activity of sulphur, they published two masterful papers in which the whole situation was studied.[2] The general ideas developed are that, as a kiln is heated, there is an evolution of water, carbon dioxide, and sulphur dioxide from the ware. That this evolution must be allowed to run to completion below 900°C and also that all iron present must be oxidized below this temperature. That in some cases an evolution of combustible gas will raise the temperature above 900°, while itself reducing the iron. In such a case the kiln must be sealed and fires banked or drawn. That above 900°C the capillaries of the clay close, preventing the further evolution of gases.[3] That if ferrous iron remains in the center of the ware, a comparatively harmless but unsightly black core of ferrous silicate will persist. That carbon is completely eliminated by oxidation in the average ceramic burn before sulphur is burnt off. That the sulphur is in reality the principal culprit, acting as a reducing agent inside the brick. That the sulphur comes off in two stages, FeS_2 becoming FeS and SO_2 and then FeS burning through $FeSO_4$ to Fe_2O_3 and SO_2. That sulphur remaining in the brick above 900° C will cause swelling.

These conclusions were reached from a ceramic point of view. In the experimental work, various clays were made up into small brick. These were burned according to good and bad firing schedules in a laboratory kiln. The gases evolved were not studied, but the samples were studied as brick and only incidental chemical analyses were made.

Mellor[4] studied the evolution of sulphur from pyrite and marcasite by heating the powdered minerals in a gentle current of air to successive temperatures. He found 6.5% of the sulphur evolved at 400°, 32.3% at 500°, and 76.2% at 600°, etc. Even at 900° there was 6.6% of the sulphur of pyrite remaining. "The powdered minerals were stirred up and a portion withdrawn for analysis at the times stated." The conditions of this experiment were so different from the case of the mineral present as a small impurity in a clay that analogy should be drawn with caution. In describing the oxidation of these minerals, Mellor states that some ferrous sulphate is formed at low temperatures in excess of air and at higher temperatures ferric and basic ferric sulphates are produced. He

[1] Orton, *Trans. Amer. Ceram. Soc.*, **5**, 331 (1903).

[2] Orton and Griffin, "The Influence of Carbon in the Burning of Clay Wares," Second Rept. of Comm. on Tech. Investigation, National Brick Manufacturers' Association (1905). Orton and Staley, "A Study of the Chemical Status of the Carbon, Iron, and Sulphur in Clays during the Various Stages of Burning," Third Rept. of same Comm. (1908).

[3] See J. M. Knote, *Trans. Amer. Ceram. Soc.*, **12**, 226 (1910).

[4] J. W. Mellor, *Trans. Ceram. Soc.* (English), **6**, 142 (1907); **7**, 112 (1908).

discusses the possible removal of pyrite by chemical, electro-magnetic, and electrostatic methods.

H. B. Wells[1] met his sulphur problem by experiments on a commercial kiln. Finding that kilns burning a high sulphur clay were producing very unsatisfactory ware, he tried drawing the fires at dull redness. Sulphides continued to burn and increase the temperature of the kiln till the center and bottom were overburnt. A forced draft of cold air did not help matters. Finally he drew fires at the first hint of sulphur fumes and opened the top of the kiln and closed the dampers. This let the sulphur in the upper part of the kiln burn off without heating the center and bottom. At the proper time the openings in the top were closed again, the dampers opened, and firing resumed. This greatly increased the uniformity of product.

Knollman[2] said that sulphuring during watersmoking seemed to be the main cause of pinholing in glazes, since it is possible to use a harder, more viscous glaze when the watersmoking period is reduced.

Stout[3] showed that iron sulphide nodules in clay were of secondary origin, and would start to form around a bit of carbon or any small grain that may start a crystalline growth.

Garve[4] said that with a limey clay, while some scum is formed in the drier, if it is burnt in a continuous kiln without advance heating flues the scumming will be worse. This can be diminished by finishing the burn under reducing conditions, thus driving off SO_3.

H. W. Hofman and W. Mostowitsch[5] showed that SiO_2 or Fe_2O_3 lowers the dissociation temperature of $CaSO_4$ to 1000° and 1100°, respectively.

A. E. Williams[6] studied the effect of atmosphere on the decomposition of calcium sulphate in a quantitative way.

J. G. Hay[7] mentions the catalytic power of colloidal clay in hydrogenizing oils, oxidizing organic compounds, etc. While far from the best catalyst, it has great advantages as a support for the real catalyst.

A. O. Jones[8] discusses the equilibrium and reaction velocity of the reaction $2SO_2 + O_2 \rightleftharpoons 2SO_3$, and reviews the work of Haber, Bodenstein, and Knietsch on this reaction.

Parmelee[9] gives a good résumé of the literature with impartial interpretation.

[1] "A Method of Overcoming the Sulphur Problem," *Trans. Amer. Ceram. Soc.*, **11,** 93 (1909).

[2] *Trans. Amer. Ceram. Soc.*, **17,** 165 (1915).

[3] *Ibid.*, **17,** 586 (1915).

[4] *Ibid.*, **17,** 600 (1915).

[5] *Trans. Inst. Min. Eng.*, **39,** 628.

[6] *Trans. Amer. Ceram. Soc.*, **17,** 764 (1915); **18,** 271 (1916).

[7] *Chem. Age*, **2,** 194 (1920).

[8] *Chem. Trade Jour.*, **69,** 183 (1921).

[9] "Soluble Salts in Clay Wares," *Brick and Clay Rec.*, Aug. 22, Sept. 2, **1922.**

Method of Attack

It was thought that an attack on the problem from a chemical point of view might open up the subject from a different angle.

The work was accordingly undertaken as a purely chemical research with only such incidental ventures into ceramics, in order to obtain fundamental data, as would serve to connect the work with the ceramic industry.

A well known fire clay was selected to begin with. This was the Lower Kittanning clay, as used at Fallston, Pennsylvania, in the manufacture of face brick. It showed the following constituents on analysis:

Loss on ignition	7.07	Lime	0.26
Silica (SiO_2)	66.18	Magnesia (MgO)	.47
Alumina (Al_2O_3)	17.19	Potash (K_2O)	1.80
Ferric oxide (Fe_2O_3)	5.10	Soda (Na_2O)	.23
Titania (TiO_2)	1.48	Sulphur (S)	.28

A number of cylindrical bars were made, three quarters of an inch in diameter and about seven inches long. They averaged about 70 grams in weight. These bars were thoroughly dried at 110°C and then were cooled and kept in a desiccator. These bars would slip into a refractory tube in an ordinary Hoskins electric tube furnace.

Such a furnace seemed eminently fitted to begin the study of oxidation of clay. Any desired temperature up to 1100°C could be attained with rapidity and maintained with considerable accuracy for long periods without attention. Any atmosphere could be supplied to a bar of clay in the tube without contamination by fuel gases. Exit gases could be passed through appropriate absorption apparatus and the various compounds thus removed quantitatively.

According to Orton, as previously mentioned, the burning reactions result in the evolution of carbon dioxide, sulphur dioxide, sulphur trioxide, and water, and the formation of ferric oxide. The study of the progress of these first three reactions was first undertaken. The evolution of water will be considered in a following paper of this series. It was planned to conduct a series of tests with varying atmospheres, using pure oxygen, pure nitrogen, and mixtures of the two in varying proportions, as well as varying percentages of carbon dioxide. In the work described in this paper, pure oxygen alone was used in the belief that reactions which proceed sluggishly under firing practice would be greatly accelerated, but not changed in nature. Under these violent oxidizing conditions and in view of the fact that clay at certain temperatures is a catalyst for the reaction, we would expect the formation and evolution of sulphur trioxide as well as sulphur dioxide. The determination of water and carbon dioxide when so evolved is solid ground. A U-tube of granular calcium chloride and a

Liebig bulb filled with 20% caustic soda solution and provided with a small guard tube of calcium chloride are conventional. The gain in weight of these gives, respectively, the amounts of water and of carbon dioxide absorbed. The system was provided with a three-way cock between combustion tube and calcium chloride tube and two absorption trains were provided so that the current of gas could be switched from one train to another without loss at appropriate intervals and the used train could then be detached, weighed, and replenished. The combustion tube was drawn down at the exit end and made as short as possible, and the limbs of the three-way cock were shortened to the limit to cut down the cooler gas space. This was done so that the water vapor would not cool and condense and be held back, but would be collected as soon after it left the clay as was the carbon dioxide. Thus the course of gas evolution could be followed.

Oxygen was passed from a tank of compressed gas through 20% caustic soda and a calcium chloride tube to the combustion tube. Tubes for various temperatures and of varying lengths were made of Jena glass, Pyrex glass and fused quartz.

All experiments of this series were started with the furnace cold. A bar of clay was weighed and put into the middle of the combustion tube. A noble metal thermocouple connected to a potentiometer was inserted between tube and furnace, oxygen turned on, rheostat set for the desired temperature, and the heating circuit completed. After an hour the current of exit gas was switched to the other train. The used train was then weighed and renewed. The train was changed every half hour at lower temperatures, every twenty minutes at higher temperatures, until the bulk of gas evolution had ceased. This rapid changing was kept up for from two and a half to four hours. During the rest of the day, the trains were changed at longer intervals and the last one was left on all night.

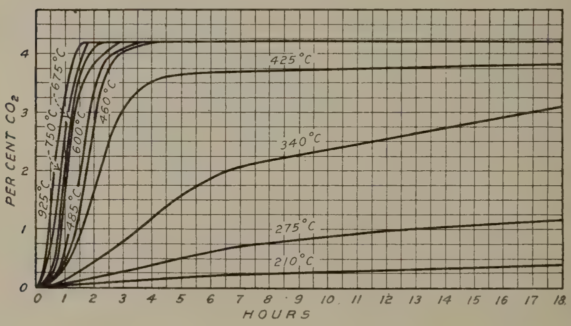

FIG. 1.

Evolution of Carbon Dioxide

The evolution of carbon dioxide is shown in Fig. 1. A very little is given off at low temperatures. The amount increases rapidly with the temperature to a definite maximum. The only difference at higher temperatures is that the maximum is reached sooner. This must be formed by the burning of carbon in the clay. Carbon may be present either as an impurity of real coal, or the clay may be a low-grade oil shale, or both.

Carbon dioxide present as carbonate in the clay was also determined by heating a weighed amount of clay in a flask with sulphuric acid and passing the gases evolved through a $CaCl_2$ tube and a weighed soda bulb. The gain in weight corresponded to 0.145% CO_2.

Evolution of Sulphur

Sulphur is also being given off, both as dioxide and as trioxide. The sulphur dioxide is all absorbed in the caustic soda solution and was determined without difficulty. Sulphur trioxide, however, is not so accommodating. It combines with water to form a sulphuric acid mist. A little of this mist may be absorbed by the wet grains of calcium chloride. Much of it is dissolved by the caustic soda solution, but traces may pass on out and be lost if its concentration is high. This can be seen, in extreme cases as a white smoke issuing from the soda bulb. Its absorbtion will be taken up in the following paper of this series. After each used caustic soda bulb had been weighed for carbon dioxide absorbed, it was washed out into a 100-cc. graduated flask and refilled with fresh caustic soda. The spent solution, containing carbonate, sulphite, and sulphate, was diluted to 100-cc. volume and divided into two equal portions. One of these portions was promptly neutralized with a slight excess of hydrochloric acid, boiled to expel the last traces of CO_2 and SO_2, and then precipitated with $BaCl_2$ solution. This brought down all of the H_2SO_4 formed from sulphur trioxide as $BaSO_4$. After standing over night, this was filtered on an ashless paper, ignited to red heat in a weighed platinum crucible, and weighed. The other portion of spent solution was neutralized with a slight excess of nitric acid. Then either hydrogen peroxide or bromine water was added. It was thought that the bromine water was more efficient. Oxidizing gases were thus retained in solution as long as

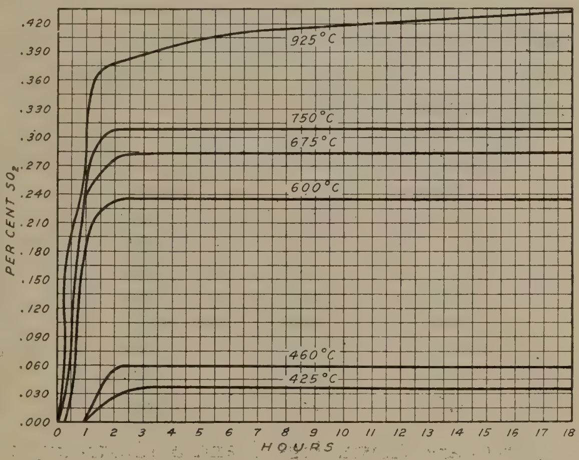

FIG. 2.

possible and all SO_2 was oxidized to SO_3. What was expected to be a slight excess of barium nitrate solution was then added. The solution was heated to boiling and boiled until colorless. More barium nitrate was then added to make sure that all of the sulphur was precipitated as $BaSO_4$. This was determined as in the previous case. Thus the weight of SO_3 and of $SO_2 + SO_3$ present were calculable. By subtraction, the weight of SO_2 was found. The weight of SO_2 and of SO_3 found in each caustic soda bulb was subtracted from the gain in weight of the bulb to give the actual weight of CO_2 present. No correction was applied to the $CaCl_2$ tubes, since the very small amount of H_2SO_4 mist absorbed practically equalled the amount of water carried on by the SO_3 as H_2SO_4.

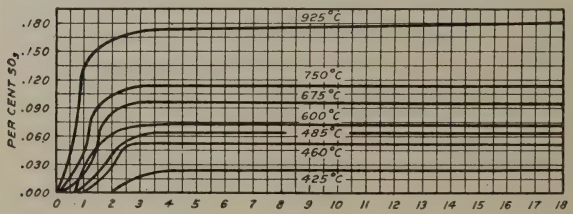

FIG. 3.

While it is thus shown that the values for sulphur found in this series of experiments do not tell quite the whole truth, still it was necessary to determine them in order to determine CO_2 and they throw much light on the subject. The figures are given below to give a close approximation of the sulphur evolved:

Temperature °	Per cent SO_2	Per cent SO_3	Per cent total S	Ratio $\frac{SO_2}{SO_3}$
340	none	none	none	none
425	none	0.0239	0.0096	0
460	0.0308	0.0500	0.0354	0.62
486	0.0574	0.0627	0.0538	0.92
500	0.0486	0.0882	0.0596	0.55
600	0.2333	0.0710	0.1450	3.29
675	0.2823	0.0954	0.1793	2.96
750	0.3090	0.1144	0.2003	2.70
925	0.4320	0.1818	0.2887	2.38

Curves are shown, Figs. 2 and 3, illustrating the rate at which SO_2 and SO_3 are evolved. It will be noticed that, except at the highest temperature no sulphur was evolved after four hours of heating. The interpretation of these results will be taken up later.

Sulphur Evolved at Varying Rates of Heating

Another line of experiment was now tried. A bar of clay was heated for four hours to 390°, then the temperature was raised to 570° for four hours and then raised to 675° for four hours more. In this test two soda bulbs were alone used in series, no calcium chloride tube, and the bulbs were changed just before the temperature was raised each time. The evolution of sulphur gases was so slow that there was never any sulphur in the second bulb. Absorption in the first was, therefore, as complete as NaOH would absorb. The total amount of sulphur evolved was as follows:

Temperature °	Per cent SO_2	Per cent SO_3	Per cent S	Ratio $\frac{SO_2}{SO_3}$
390	none	0.0184	0.0074	0
570	0.0283	0.0935	0.0515	0.30
675	0.0589	0.1075	0.0724	0.55

This shows that only 0.724% of sulphur was given off in this whole 12 hours heating up to 675° while in the previous test to the same temperature 0.1793% was evolved. Notice also that in the normal test the $SO_2:SO_3$ ratio is about 3.0 and in the slowly increased temperature this ratio is 0.55. The slow evolution of gas in the presence of pure oxygen would account for this excess of SO_3.

The third series of experiments was made also on this subject. A bar of clay was heated to 505° for four hours and the sulphur gases caught and analyzed as before. A new soda bulb was then put on and a new bar of clay was placed in the hot tube in addition to this first bar and oxygen passed for four hours more. Sulphur gases were again collected and determined. The furnace was cooled and the bars removed. It was then heated empty to 505°, oxygen passed till the air was displaced, a soda bulb put on and a weighed bar of clay inserted in the tube. A stream of oxygen was passed for four hours and the sulphur gases caught and analyzed as before. The results were as follows:

State of furnace at start	Temperature °	Per cent SO_2	Per cent SO_3	Per cent S	Ratio $\frac{SO_2}{SO_3}$
Cold, empty	505	0.0862	0.0538	0.0646	1.6
Hot, one bar in	505	0.1259	0.0272	0.0738	4.6
Hot, empty	505	0.1984	0.1226	0.1482	1.6

These figures are astounding. More than twice as much sulphur is given off in the third case as in the first. Yet the ratio of $SO_2:SO_3$ is the same. The only difference between the cases was the rapidity with which the clay was heated. Therefore, this increase in evolved sulphur must be due to this cause. As much sulphur must have been evolved from the second bar as from the third, since conditions were identical. The only place that the sulphur could have disappeared to was into the first bar, which was still in the furnace. This first bar must then have absorbed the amount of sulphur equal to the difference between that given off by the second and that given off by the third bar. This difference, .0744% S, is greater than the amount of sulphur previously evolved by the first bar. The investigation of this question called for a fourth series of experiments.

Analysis of Clay Bars

A typical series of partly burned clay bars was selected for analysis. No. 1 had been dried at 110°, but had had no other heat treatment. No. 2 had been heated to 485° for 20 hours. No. 3 had been heated to 505° for eight hours. During four of these hours there was another bar behind it. No. 3 was the first case in the previous experiment. No. 4 had been put into a preheated furnace and held at 505° for four hours. It was the third case in the previous experiment. No. 5 had been heated to 600°, No. 6 to 675°, No. 7 to 750° and No. 8 to 925°, each for approximately twenty hours in oxygen. Ten grams of each body were finely ground, accurately weighed, and then boiled with 150 cc. distilled water for half an hour. On settling, the water was poured off and the clays washed twice by decantation. The water and washings were then analyzed for sulphur. The clays were boiled for half an hour more each with 150 cc. of 1–5 hydrochloric acid solution. This was in turn poured off, the clays each washed twice, and the washings and acid solution tested as before. The clays were then boiled with 1–3 nitric acid and the process repeated. Sulphur was determined as $BaSO_4$, as in the previous work.

			Cold start	Hot start				
T° of previous heating	110°	485°	505°	505°	600°	675°	750°	925°
Per cent S evolved by heat	none	0.0538	0.0646	0.1482	0.1450	0.1793	0.2003	0.2887
Per cent S dissolved by water	0.040	0.129	0.238	0.150	0.097	0.046	0.034	0.007
Per cent S dissolved by 1–5 HCl	none	0.116	0.059	0.006	0.050	0.041	0.026	0.001
Per cent S dissolved by 1–3 HNO_3	none	none	none	none	none	none	none	none
Total per cent S found	0.040	0.299	0.362	0.304	0.292	0.266	0.260	0.297

Discussion of Results

In the case of the raw clay, most of the sulphur remains undissolved, as pyrite. The soluble sulphur may be referred to sulphates of alkalies, alkaline earths, or iron. In the second case, as much sulphur was found evolved or dissolved as in the other normal cases. This shows that the reaction

$$FeS_2 + O_2 = FeS + SO_2 \text{ or } 2FeS_2 + 3O_2 = 2FeS + 2SO_3 \qquad (1)$$

has proceeded to completion. FeS is insoluble in water, but soluble in HCl solution. It will be noticed that the amount of sulphur extracted by HCl solution is less the higher the temperature. This means that the FeS has been changed by oxygen and heat in one or more of the following ways:

$$\begin{aligned} 4FeS + 7O_2 &= 2Fe_2O_3 + 4SO_2 \\ 4FeS + 9O_2 &= 2Fe_2O_3 + 4SO_3 \\ FeS + 2O_2 &= FeSO_4 \\ 2FeS + 5O_2 + SO_2 &= Fe_2(SO_4)_3 \end{aligned} \qquad (2)$$

There is also a possibility of a direct oxidation of pyrite:

$$\begin{aligned} 2FeS_2 + 7O_2 &= Fe_2(SO_4)_3 + SO_2 \text{ or} \\ 4FeS_2 + 15O_2 &= 2Fe_2(SO_4)_3 + 2SO_3 \\ FeS_2 + 3O_2 &= FeSO_4 + SO_2 \\ 2FeS_2 + 7O_2 &= 2FeSO_4 + 2SO_3 \end{aligned} \qquad (3)$$

To this particular clay, about 5% of iron as mill scale had been added for commercial purposes. This iron, when hot and wet with evolved water of constitution, will readily absorb SO_2 and SO_3 to form sulphate:

$$\begin{aligned} Fe + SO_2 + O_2 &= FeSO_4 \\ 2Fe + 2SO_3 + O_2 &= 2FeSO_4 \\ 2Fe + 3SO_2 + 3O_2 &= Fe_2(SO_4)_3 \\ 4Fe + 6SO_3 + 3O_2 &= 2Fe_2(SO_4)_3 \end{aligned} \qquad (4)$$

Either gas may form either sulphate. These sulphates form the sulphur dissolved in water. Their amount decreases as the temperature increases, and they are decomposed by the reversing of the above reactions and the oxidation of the iron.

In the third case in the table above, this water soluble sulphur is very high since sulphur gases from a second bar of clay were also absorbed by the iron. That this has happened is proved by the fact that the total per cent of sulphur found is 20% above normal. In the fourth case above, the rapid heating formed very little ferrous sulphide. The action was so rapid that oxygen was probably scarce and the reaction taking least oxygen, namely that forming ferrous sulphate directly from pyrite, predominated. The SO_2 was generated so rapidly that comparatively little was taken up again by the iron, making a high yield of sulphur-bearing gases.

Conclusions

The following tentative conclusions would seem to be justified. Further work proving or disproving them, will be necessary before they may be considered final.

1. That carbon is burnt out completely by oxygen at 460°.
2. That it is burnt out more rapidly the more rapid the rate of heating.
3. That sulphur is evolved as dioxide and trioxide the more rapidly the faster and the higher the heating is carried out. Sulphur evolution is practically complete at 925°C after prolonged heating.
4. That at a temperature of 485° in oxygen the decomposition of FeS_2 appears to be complete.
5. That at temperatures of 505° and below, the principal source of

sulphur evolution seems to be the oxidation of FeS_2 to FeS, forming SO_3 and SO_2.

6. That while half of the total sulphur is thus dislodged at low temperatures and forms gases, much of these gases are again absorbed by impurities in the clay as sulphates.

7. That the amount of re-absorption of these gases is greater the more slowly they are evolved.

8. That the FeS formed by the decomposition of FeS_2 must further decompose to form either Fe_2O_3 and sulphur gases or else to form sulphate. The choice of action will depend on the rate of heating and the temperature attained.

9. That in an atmosphere of oxygen practically all FeS is oxidized one way or the other by a temperature of 500°.

10. That the decomposition of the remaining sulphates proceeds progressively to completion between 600° and 925°. Calcium sulphate is not considered in this connection.

Further work will develop more fully various phases of this entire subject and papers on the same general subject will be published from time to time. It is planned eventually to review them all and to tie up the loose ends in a general series of conclusions.

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COMBUSTION IN KILNS BURNING REFRACTORY WARE[1]

By Ralph A. Sherman[2]

ABSTRACT

The results are presented of a study of the process of combustion in kilns burning refractory wares, using coal as fuel. The work was undertaken in connection with the investigation of burning problems in the manufacture of refractories, conducted by the Bureau of Mines in coöperation with the Refractories Manufacturers Association.

Combustion in a Kiln

In a brick kiln the coal is burned in a number of fire-boxes placed about the periphery. The coal may be supported on inclined or flat grate bars or may rest on the bottom of the fire-box as in the "dead-bottom" type. Doors to close the opening through which the coal is fired are not commonly used, the fresh charges of coal filling this opening. The firing opening thus serves as an additional grate area.

The combustion of coal in a fuel bed takes place in three stages. The first stage is the union of the oxygen of the air with the carbon of the coal to form carbon dioxide. This reaction is very rapid and takes place in the first few inches from the point of air admission. The second stage is the union of the carbon dioxide, so formed, with more carbon to form carbon monoxide. The third stage is the distillation of the volatile matter from the freshly fired coal at the top of the fuel bed. The volatile matter leaves the fuel bed in the form of various gaseous hydrocarbons and tar. Thus the fuel bed is divided into three zones which, however, are not distinct, but overlap.

The gases arising from a fuel bed, therefore, are carbon dioxide, nitrogen, carbon monoxide, hydrogen, methane, and other hydrocarbons, together with solid tar and soot. It has been shown[3] that no oxygen can pass through a level incandescent fuel bed 4 to 6 inches thick. The fuel beds in the furnaces of brick kilns are ordinarily carried at a thickness of from 18 inches to 3 feet. Therefore, oxygen must be admitted to burn the combustible arising from the fuel bed. This oxygen comes through the cool and thin bed of coal at the firing opening and through "eyes" in the wall above the fire-boxes.

The reaction of oxygen with the gaseous combustibles to form carbon dioxide and water is much less rapid than with solid carbon as in the fuel bed but will take place quickly if the gases are thoroughly mixed and a high temperature is maintained in the combustion chamber. The more thorough the mixing the lower is the excess of air required for complete combustion of the gases in a given distance.

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[1] Published by permission of the Director, U. S. Bureau of Mines. Presented at the Atlantic City Meeting, February, 1924. (Refractories Division.)

[2] Assistant Physicist, Pittsburgh Experiment Station, Bureau of Mines.

[3] Henry Kreisinger, F. K. Ovitz, C. E. Augustine, "Combustion in the Fuel Bed of Hand-Fired Furnaces," Bur. Mines, *Tech. Paper* **137,** 9 (1917). The reader is referred to this paper for a thorough discussion of the process of combustion in the fuel bed.

The complex gaseous compounds of carbon and hydrogen and the tar may burn to carbon dioxide and water directly without decomposition if they are distilled in the presence of oxygen. In the absence of oxygen they will be decomposed by the heat of the furnace into simpler compounds with the liberation of free carbon or soot.

Although the reaction between these carbon particles and oxygen is that of a solid and a gas it is extremely slow. This is doubtless due to the fact that the light particles are carried along in the gas stream at practically the same velocity as the gas. There is no scrubbing action of the gas on the surface of the particle and thus any carbon dioxide formed remains around the particle as a protective film through which oxygen for further combustion can penetrate only by the slow process of diffusion. Therefore free carbon will persist unburned for a great distance even in the presence of a considerable excess of oxygen over the amount theoretically required for combustion. These incandescent carbon particles give the flame its luminosity.

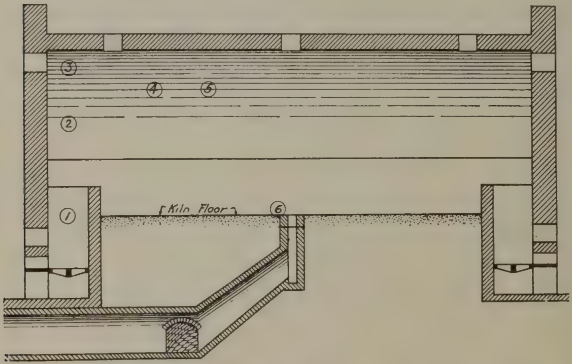

Fig. 1.—Section of rectangular kiln. Circles indicate position of samples.

If large amounts of combustible gases could be formed in the furnaces of a brick kiln and their combustion delayed until they approached the center and bottom of the setting less heat would be liberated near the rims and top of the ware and over-burning avoided while more would be liberated near the points which are difficult to heat. Thus a more uniform temperature would be attained throughout the kiln.

The purpose of this investigation was to determine, by the sampling and analysis of the gases along their path of travel through the kiln, the extent of the combustion zone in a kiln.

Scope of Investigation

The investigation was conducted on two types of kilns: (1) A rectangular, end-fired, down-draft kiln with one central transverse flue, commonly known as the "Newcastle" kiln. (2) A round down-draft kiln with fully perforated bottom. The leading dimensions and particulars of these kilns are given in Table I.

Samples were taken during two successive burns on each kiln. Some changes in the setting and the method of firing were adopted for the second burn as were deemed advisable from observations on the first burn.

Method of Investigation

Water-cooled gas samplers were inserted in the kilns at the positions shown in Figs. 1 and 2. These positions were selected as representative positions and as possibly being in the path of the gas stream so that the progress of combustion could be followed from point to point.

TABLE I

DIMENSIONS AND PARTICULARS OF KILNS

General particulars	Units	Kiln	Kiln
1. Type of kiln		Rectangular end-fired	Round
Kiln Dimensions			
2. Inside	Ft.-in.	16–6 x 30–6	Diameter 25 ft.
3. Height to top of crown	Ft.-in.	10–4	15–6
Furnaces			
4. Type		Flat grates	Dead bottom
5. Number		6	10
6. Dimensions			
(*a*) First burn	Inches	22 x 30	23 x 40
(*b*) Second burn	Inches	36 x 30	......
7. Area poking door	Sq. in.	198	......
8. Effective grate area			
(*a*) First burn	Sq. in.	858	391[1]
(*b*) Second burn	Sq. in.	1278	......
9. Area firing opening	Sq. in.	308	207
10. Ratio firing area to effective grate area			
(*a*) First burn		0.36	0.53
(*b*) Second burn		0.24	......
Stack Dimensions			
11. Cross-section	Inches	24 x 24	37 x 37
12. Height	Ft.	37	41
13. Capacity of kiln	Pieces	......	......
	9″ equivalents	40,000	40,000
Time of Burn			
14. First burn	Hours	156	83½
15. Second burn	Hours	134½	80

[1] Area of ash pit opening.

The gases were drawn in a continuous stream by means of a motor driven pump and a portion of this stream was collected at a uniform rate by displacement over a saturated salt solution. The samples were drawn simultaneously from the several positions over periods of from 10 minutes to one hour.

The composition of the samples was determined by analysis in an Orsat using mercury as the displacing fluid, the carbon dioxide, oxygen, carbon monoxide, hydrogen, and methane contents being determined.

The temperature of the gases in the furnace was determined by means of an exposed platinum, platinum-rhodium thermocouple. The other temperatures in the kiln are the temperatures of the ware near the points of sampling. The temperature and composition of the stack gases were taken from the regular data recorded during the burns. The stack gas samples were drawn during a half or one-hour period and were, therefore, not simultaneous with the samples drawn from the kiln.

The pressures were taken by means of an inclined draft gage attached to a pipe inserted in the kiln near the points of sampling.

The composition of the gas samples, the temperatures, pressures, and remarks are given in Table II.

Discussion of the Results

Rectangular Kiln.—The burning method followed during the first burn of this kiln was that of the usual plant practice. After the period of water smoking the fires were carried very heavy, varying from about two feet at the front of the fire-boxes to three feet or more at the back. The firing opening was more or less stopped with green coal according to the speed at which it was desired to raise the temperature.

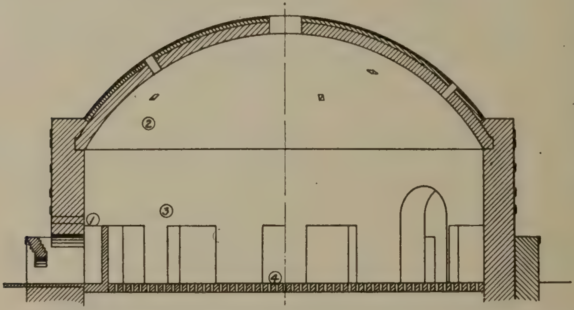

FIG. 2.—Section of round kiln. Circles indicate positions of samplers.

The gases at position 1, just above the fuel bed, were, in general, of higher oxygen content than those at position 2 indicating that this sampler was in an air stream coming through the firing door and that the gases passed upward farther toward the setting. An appreciable content of combustible gases was found in but one set of samples, set 4, at this position and this had almost completely disappeared at position 2. The presence of small amounts of carbon monoxide in the samples from other positions is probably owing to the fact that for a few minutes after firing there was insufficient air admitted to completely burn the gases. As the samples were drawn over a half-hour period the carbon monoxide appeared as small percentages in the sample. This also explains the presence of appreciable amounts of this combustible gas together with oxygen in the samples taken from the stack when they were drawn over periods of one hour.

For the second burn on this kiln the setting was opened somewhat, the grate area was enlarged, and steel plates were hung over the firing openings to reduce the excess air during the water smoking period. These temporary doors were effective as is shown by the lower excess air in samples of set 1 than in those of a corresponding period in the first burn. Later, however, they became warped by the heat and were less effective in reducing excess air than stoppage of the openings by green coal.

The second set of samples was taken during the first ten minutes after firing. The sample from position 1 contained but 0.6% of oxygen with 2.5, 2.6, and 1.0% of carbon monoxide, hydrogen, and methane, respectively. The combustible content of the gases is lower at position 2 showing that oxygen has been supplied in addition to that present at position 1. This doubtless came from the other fire-boxes. Additional air met the gas stream to reduce the combustible content at the top of the kiln, position 4, and at the bottom center there is practically no combustible and an excess of oxygen. The significance of these samples is the very rapid combustion of carbon monoxide in the kiln when supplied with the necessary amount of oxygen.

The samples of sets 6, 7, 8, and 9, which cover a firing cycle of $1^3/_4$ hours, together with furnace gas temperatures, show very clearly the changing conditions in the kiln during the cycle. Immediately after firing there is a very heavy evolution of volatile matter giving in the furnace gases 10.4 and 8.0% of carbon monoxide and hydrogen, respectively, which are reduced before position 2 by an additional air supply to 6.0 and 2.8%. In the following half-hour period the combustible gases were greatly diminished and the carbon dioxide content in the furnace gases had risen to 15%. During the next two periods the coal which had stopped the firing doors had burned down admitting a greater supply of air and the combustible consequently disappeared and the carbon dioxide decreased.

The furnace gas temperatures follow the gas composition very closely. Shortly after firing, the temperature was low, 2274°, owing to the deficiency in air supply, then, as the air supply increased, rose to a maximum of 2529°, 40 minutes after firing, then fell to 2159° owing to the increasing excess of air.

During the period covered by sets 10, 11, 12, and 13, the fires were carried more open and the gas composition and temperatures were more uniform than when the fires were tightly closed on firing.

The pressure at any point in the kiln, except immediately above the fire-boxes and at the bottom of the kiln, was greater than that of the air at the same level.

TABLE II

RESULTS OF INVESTIGATION, RECTANGULAR KILN, FIRST BURN

Set no.	Hour of burn	Time of sample	Position of sample	Composition of gas					Temp., °F	Pressure in water	Remarks
				CO_2	O_2	CO	H_2	CH_4	N_2			
			1	1.7	17.5	0.0	0.0	0.0	80.8	..	....	
		10.40 A.M.	2	2.4	16.5	0.5	0.0	0.0	80.6	..	....	Fired 10:30 A.M.
1	17	to	3	3.8	15.4	1.4	0.0	0.0	79.4	..	....	6″–8″ below arch
		11:40 A.M.	4	3.5	15.8	0.4	0.0	0.0	80.3	521	....	
			5	3.9	14.7	0.3	0.0	0.0	81.1	..	....	
			6	3.6	15.0	0.0	0.0	0.0	81.4	298	....	
			Stack	5.6	13.8	0.0	0.0	0.0	80.6	171	– .054	
			1	5.7	13.4	0.4	0.0	0.0	80.5	..	....	
		9:40 A.M.	2	10.8	7.6	0.4	0.0	0.0	81.2	..	....	Fired 9:30 A.M.
			3	12.0	6.2	0.4	0.0	0.0	81.4	..	....	1″–3″ below arch
2	40	to	4	13.2	5.8	0.0	0.0	0.0	81.0	1489	.036	
			5	12.2	6.3	0.2	0.0	0.0	81.3	..	.034	
		10:30 A.M.	6	12.5	6.3	0.0	0.0	0.0	81.2	958	– .012	
			Stack	12.8	6.2	0.0	0.0	0.0	81.0	569	– .150	
			1	5.0	13.3	0.2	0.0	0.0	81.5	..	....	
		9:20 P.M.	2	6.8	11.9	0.0	0.0	0.0	81.3	..	....	Cleaned fires
			3	6.2	13.0	0.2	0.0	0.0	80.6	..	....	8–9:20 P.M. fired
3	51	to	4	8.4	9.9	0.1	0.0	0.0	81.6	1543	....	close up to arch
			5	8.3	9.7	0.0	0.0	0.0	82.0	..	....	
		9:50 P.M.	6	8.0	8.8	0.3	0.0	0.0	82.9	1198	....	
			Stack	8.6	10.2	0.2	0.0	0.0	81.0	725	– .190	
			1	12.1	1.9	7.0	1.6	1.5	75.9	..	– .045	
		10:45 A.M.	2	15.9	2.4	0.3	0.0	0.0	81.4	..	.022	Fired 10:30 A.M.
			3	16.4	1.1	0.9	0.3	0.0	81.2	..	.020	fired close up to arch
4	65	to	4	17.8	0.2	0.4	0.0	0.2	81.6	1947	.000	
			5	17.3	0.6	0.3	0.2	0.0	81.6	..	.001	
		11:15 A.M.	6	17.6	0.3	0.5	0.2	0.2	81.2	1749	– .053	
			Stack	15.0	4.2	0.0	0.0	0.0	81.8	..	– .200	
			1	5.2	13.8	0.2	0.0	0.0	80.8	..	.071	
		2:45 P.M.	2	11.3	6.6	0.0	0.0	0.0	82.1	..	.028	Fired 2:30 P.M.
			3	13.1	4.0	0.2	0.0	0.0	82.7	..	.070	2″–4″ below arch

Table II (*Continued*)

5	69	to	4	12.9	3.2	0.2	0.0	0.0	83.7	2042	.021	
			5	12.4	4.3	0.2	0.0	0.0	83.1	..	.019	
		3:15 P.M.	6	14.7	1.1	0.0	0.0	0.0	84.2	1849	– .030	
			Stack	14.8	4.0	0.0	0.0	0.0	81.2	1052	– .200	
			1	9.5	9.0	0.0	0.0	0.0	81.5	..	.195	
		11:00 A.M.	2	12.1	6.0	0.0	0.0	0.0	81.9	..	.075	Fired 10:45 A.M.
			3	12.2	5.8	0.0	0.0	0.0	82.0	..	.070	3″–4″ below arch
6	89	to	4	..	..	...	...	...	..	..	....	North end fired close
			5	..	..	...	...	...	..	..	....	
		11:30 A.M.	6	..	..	...	...	...	..	..	....	
			Stack	14.2	4.8	0.0	0.0	0.0	81.0	1367	– .210	
			1	4.8	13.9	0.3	0.0	0.0	81.0	..	.095	
		2:45 P.M.	2	14.2	1.2	1.0	0.6	0.0	83.0	..	.030	Fired 2:30 P.M.
			3	11.8	4.0	0.2	0.0	0.0	84.0	..	.045	2″–3″ below arch
7	93	to	4	..	..	...	...	...	..	..	....	
			5	12.9	2.6	0.0	0.0	0.0	84.5	..	.030	
		3:15 P.M.	6	14.1	0.5	0.3	0.5	0.2	84.4	2116	....	
			Stack	13.4	5.4	0.0	0.0	0.0	81.2	1430	– .215	
			1	14.4	4.7	0.2	0.5	0.0	80.2	..	– .010	
		9:30 A.M.	2	15.5	4.1	0.0	0.0	0.0	80.4	..	.040	Fired 9:15 A.M.
			3	13.9	4.9	0.3	0.0	0.0	80.9	..	.090	close to arch
8	112	to	4	15.1	3.5	0.1	0.0	0.0	81.3	2203	.070	No. 4 and No. 5 samplers 1′
			5	14.4	3.8	0.0	0.0	0.0	81.8	..	.060	inside crown No. 6
		9:50 A.M.	6	14.6	3.2	0.0	0.0	0.0	82.2	2147	.020	7′ inside crown
			Stack	13.2	5.6	0.0	0.0	0.0	81.2	1595	– .210	
			1	11.1	7.0	0.0	0.0	0.0	81.9	..	– .025	
		10:50 A.M.	2	14.6	3.2	0.0	0.0	0.0	82.3	..	.035	Fired 10:30 A.M. close to arch
			3	14.5	3.4	0.0	0.0	0.0	82.1	..	.060	No. 4 sampler not in,
9	137	to	4	..	..	..	...	...	..	..	....	others as in set 8
			5	13.2	3.3	0.1	0.0	0.0	83.4	..	.040	
		11:15 A.M.	6	14.9	0.9	0.5	0.4	0.0	83.3	2193	.000	
			Stack	14.8	3.6	0.1	0.0	0.0	81.5	1813	– .220	

TABLE II

RESULTS OF INVESTIGATION (*continued*), ROUND KILN

First Burn

Set no.	Hour of burn	Time of sample	Position of sample	Composition of gas CO_2	O_2	CO	H_2	CH_4	N_2	Temp., °F	Pressure in water	Remarks
1	42	9:15 A.M. to 9:30 A.M.	1	7.6	11.7	0.4	0.0	0.0	80.3	..	....	Fired at 9:30 A.M.
			2	11.6	6.8	0.2	0.0	0.0	81.4	1263	....	
			3	14.5	4.8	0.0	0.0	0.0	80.7	..	....	
			4	14.5	4.2	0.3	0.0	0.0	81.0	826	....	
2	42	9:30 A.M. to 9:45 A.M.	1	5.1	14.1	0.5	0.0	0.0	80.2	..	....	
			2	11.4	7.7	0.0	0.0	0.0	80.9	..	+.038	
			3	13.0	4.7	0.5	0.0	0.0	81.8	..	−.036	
			4	15.8	2.6	0.3	0.0	0.0	81.3	..	−.072	
			Stack	13.1	5.1	0.0	0.0	0.0	81.8	583	−.255	Stack analysis 8:30–9:30
3	48	3:00 P.M. to 3:10 P.M.	1	13.2	2.3	2.7	1.1	0.0	80.7	..	....	Fired 3:00 P.M.
			2	14.7	2.1	1.5	0.3	0.0	81.7	1723	....	
			3	17.4	0.3	0.7	0.0	0.0	81.6	..	....	
			4	13.9	4.0	0.2	0.0	0.0	81.9	942	....	
4	48	3:15 P.M. to 3:25 P.M.	1	13.0	5.4	0.2	0.0	0.0	81.4	..	....	
			2	12.7	6.0	0.3	0.0	0.0	81.0	..	+.030	
			3	13.3	6.6	0.0	0.0	0.0	80.1	..	−.045	
			4	10.9	5.3	0.3	0.0	0.0	83.5	..	−.085	
			Stack	13.2	4.9	0.0	0.0	0.0	81.9	686	−.275	Stack analysis 2:30–3:30
5	67	10:15 A.M. to 10:30 A.M.	1	12.9	5.5	0.2	0.0	0.0	81.4	..	....	Fired 10:15 A.M.
			2	12.9	5.6	0.0	0.0	0.0	81.5	1849	....	
			3	12.6	6.1	0.2	0.0	0.0	81.1	..	....	
			4	11.8	7.3	0.0	0.0	0.0	80.9	1692	....	
6	67	10:34 A.M. to 10:45 A.M.	1	12.1	6.5	0.0	0.0	0.0	81.4	..	....	
			2	10.3	9.0	0.5	0.0	0.0	80.2	..	−.015	
			3	11.5	7.1	0.0	0.0	0.0	81.4	..	−.066	
			4	12.5	6.3	0.0	0.0	0.0	81.2	..	−.104	
			Stack	13.3	5.6	0.0	0.0	0.0	81.1	1122	−.370	Stack analysis 10:30–11:30

TABLE II (*Continued*)

Second Burn

1	39	7:00 A.M. to 7:15 A.M.	1	13.8	3.9	0.2	0.0	0.0	82.1	..	....	Cleaned fires 6:30 A.M. to 6:55 A.M.
			2	11.9	5.6	0.2	0.0	0.0	82.3	1226	....	
			3	11.8	6.5	0.0	0.0	0.0	81.7	..	....	
			4	10.1	7.7	0.0	0.0	0.0	82.2	515	....	
2	39	7:15 A.M. to 7:30 A.M.	1	11.9	6.7	0.2	0.0	0.0	81.2	..	−.022	Fired 7:15 A.M.
			2	11.3	7.3	0.2	0.0	0.0	81.2	..	+.048	
			3	9.9	8.8	0.2	0.0	0.0	81.1	..	−.020	
			4	8.8	9.9	0.2	0.0	0.0	81.1	..	−.054	
			Stack	9.4	8.8	0.0	0.0	0.0	81.8	500	−.230	Stack analysis 7:15–7:45
3	45	1:40 P.M. to 1:50 P.M.	1	12.6	6.1	0.0	0.0	0.0	81.3	..	....	Fired 1:45 P.M.
			2	10.0	9.5	0.0	0.0	0.0	80.5	1418	....	
			3	11.8	7.8	0.0	0.0	0.0	80.4	..	....	
			4	11.8	7.2	0.0	0.0	0.0	81.0	687	....	
4	45	1:50 P.M. to 2:00 P.M.	1	11.7	7.6	0.0	0.0	0.0	80.7	..	−.052	
			2	7.2	12.4	0.0	0.0	0.0	80.4	..	+.031	
			3	10.9	8.8	0.0	0.0	0.0	80.3	..	−.050	
			4	9.1	10.2	0.0	0.0	0.0	80.7	..	−.095	
			Stack	10.1	9.3	0.0	0.0	0.0	80.6	643	−.275	Stack analysis 1:45–2:15
5	65	9:00 A.M. to 9:10 A.M.	1	15.0	4.5	0.6	0.0	0.0	79.9	..	....	Fired 8:45 A.M.
			2	16.0	2.3	0.0	0.0	0.0	81.7	1962	....	
			3	15.4	1.6	0.0	0.0	0.0	83.0	..	....	
			4	15.3	2.6	0.0	0.0	0.0	82.1	1486	....	
6	65	9:18 A.M. to 9:30 A.M.	1	15.2	0.2	3.5	1.4	0.0	79.7	..	−.032	Fired 9:15 A.M.
			2	15.8	2.3	0.2	0.0	0.0	81.7	..	+.036	
			3	15.2	2.2	0.0	0.0	0.0	82.6	..	−.060	
			4	16.3	1.6	0.0	0.0	0.0	82.1	..	−.072	
			Stack	14.3	3.5	0.2	0.0	0.0	82.0	1065	−.360	Stack analysis 9:15–9:45

TABLE II

RESULTS OF INVESTIGATION (*continued*), RECTANGULAR KILN, SECOND BURN

Set no.	Hour of burn	Time of sample	Position of sample	Composition of gas CO_2	O_2	CO	H_2	CH_4	N_2	Temp., °F	Pressure in water	Furnace gas temp. Time	°F	Remarks
1	23	2:15 P.M. to 2:50 P.M.	1	10.4	8.0	0.6	0.7	0.0	80.3	..	....	...	..	
			2	9.6	8.4	0.0	0.1	0.0	81.9	..	....	...	..	18 inch fuel bed
			4	9.9	8.3	0.2	0.0	0.0	81.6	967	....	...	..	Steel doors on fire boxes
			6	9.4	8.0	0.4	0.0	0.0	82.2	785	....	...	..	Fired 1:30. Broke fires 2:30
			Stack	8.2	10.6	0.0	0.0	0.0	81.2	466	−.056	...	..	
2	42	9:07 A.M. to 9:17 A.M.	1	13.2	0.6	2.5	2.6	1.0	80.1	..	−.025	...	..	18 inch fuel bed
			2	14.4	0.2	2.1	1.1	0.6	81.6	..	+.025	...	..	Doors on fire boxes
			4	14.9	0.7	0.8	0.2	0.2	83.2	1544	+.035	...	..	Fired south side
			6	12.1	4.9	0.3	0.0	0.0	82.7	1312	−.030	...	..	9:00 to 9:05
			Stack	9.6	9.2	0.0	0.0	0.0	81.2	769	−.190	...	..	
3	46	1:38 P.M. to 2:06 P.M.	1	9.0	8.5	0.0	0.2	0.0	82.3	..	....	...	..	18 inch fuel bed
			2	10.1	9.0	0.3	0.0	0.0	80.6	..	....	...	..	Doors on
			4	13.1	5.0	0.2	0.0	0.0	81.7	..	....	...	..	Fired 1:30 to 1:38
			6	11.7	6.1	0.0	0.0	0.0	82.2	..	....	...	..	
			Stack	..	..	...	...	...	..	..	....	...	..	
4	46	2:09 P.M. to 2:34 P.M.	1	2.9	10.8	0.0	0.0	0.0	86.3	..	....	...	..	
			2	5.8	11.4	0.0	0.0	0.0	82.8	..	....	...	..	
			4	2.8	9.7	0.0	0.0	0.0	87.5	..	....	...	..	
			6	5.0	9.1	0.2	0.0	0.0	85.7	..	....	...	..	
5	46	2:37 P.M. to 2:57 P.M.	1	3.1	14.4	0.0	0.0	0.0	82.5	..	....	...	..	
			2	5.1	13.3	0.2	0.0	0.0	81.4	...	....	...	..	
			4	7.9	10.4	0.2	0.0	0.0	81.5	1668	....	...	..	
			6	4.4	10.8	0.2	0.0	0.0	84.6	1470	....	...	..	
			Stack	13.3	4.7	0.2	0.0	0.0	81.8	834	−.190	...	..	Stack gas 1:30 P.M.-2:30 P.M.
			1	9.8	0.2	10.4	8.0	0.4	71.2	..	....	...	..	30 inch fuel bed
		10:05 A.M.	2	13.0	0.2	6.0	2.8	0.3	77.7	..	....	10:14	2274	No doors

TABLE II (*Concluded*)

6	67	to	4	..	..	...	...	...	..	2209	....	10:26	2401	Fired 10:00 A.M. open
		10:33 A.M.	6	..	..	...	...	...	..	2024	....	10:40	2529	slightly
		10:35 A.M.	1	15.0	0.9	1.8	0.8	0.1	81.4	..	....	10:50	2401	
7	67	to	2	15.4	1.8	0.3	0.0	0.0	82.5	..	....	11:00	2388	
		11:00 A.M.	Stack	16.4	0.8	0.8	0.0	0.0	82.0	1226	—.215	11:10	2388	Stack gas 67th hour
		11:00 A.M.	1	12.5	5.6	0.2	0.2	0.1	81.4	..	....	11:20	2327	
8	68	to												
		11:30 A.M.	2	12.0	6.8	0.0	0.0	0.0	81.2	..	....	11:30	2162	
		11:30 A.M.	1	12.1	5.7	0.0	0.0	0.0	82.2	..	....	11:40	2159	
9	68	to	2	9.9	9.0	0.0	0.0	0.0	81.1	..	....	...	..	
		11:45 A.M.	6	..	..	...	...	...	..	1924	....	...	..	
			Stack	16.4	0.9	0.8	0.0	0.0	81.9	1239	—.205	...	..	Stack gas 68th hour
		10:20 A.M.	1	14.8	2.2	2.3	1.0	0.1	79.6	..	....	...	..	30 inch fuel bed
10	103	to	2	16.2	0.5	2.5	0.9	0.0	79.9	..	....	10:20	2388	Fired 10:05 to 10:20
		10:45 A.M.	6	14.3	1.9	1.3	0.7	0.2	81.6	2212	....	10:31	2401	Open 2″ to 3″
			4	..	..	...	...	...	..	2253	....	10:40	2314	
		10:45 A.M.	1	13.4	3.8	0.8	0.0	0.1	81.9	..	....	10:50	2361	
11	103	to	2	15.2	2.4	0.1	0.0	0.0	82.3	..	....	11:00	2401	
		11:10 A.M.	6	13.0	3.5	0.0	0.0	0.0	83.5	..	....	11:10	2327	
			Stack	15.8	2.0	0.2	0.0	0.0	82.0	..	—.235	11:20	2321	Stack gas 103rd hour
		11:10 A.M.	1	10.7	7.5	0.0	0.0	0.0	81.8	..	....	11:30	2334	
12	104	to	2	12.2	6.5	0.0	0.0	0.0	81.3	..	...	11:40	2334	
		11:35 A.M.	4	..	..	...	...	...	..	2250	....	11:50	2360	
			6	12.6	4.9	0.0	0.0	0.0	82.5	2233	....	...	..	
		11:35 A.M.	1	12.8	5.8	0.0	0.0	0.0	81.4	..	....	...	..	
13	104	to	2	10.7	8.1	0.0	0.0	0.0	81.2	..	....	...	..	
		11:50 A.M.	6	12.0	6.2	0.0	0.0	0.0	81.8	..	....	...	..	
			Stack	13.6	5.5	0.0	0.0	0.0	80.9	..	—.230	...	..	Stack gas 104th hour

Round Kiln.—The most significant feature of the composition of the gases in this kiln is the absence of any large amounts of combustible gases. The carbon monoxide content of the gases from above the fire-boxes was greater than 1% but twice.

This absence of combustible in the gases from the fire-boxes was due to: (1) rapid combustion in the fire-box, (2) escape of combustible gases outside the kiln.

The rapid combustion in the fire-box was caused by a large air supply per unit mass of combustible gases arising from the fuel bed. Assuming similar depths of fuel beds and the firing openings completely closed with green coal in the furnaces of the two kilns, the ratio of secondary air supply to combustible would be greater for the round than for the rectangular kiln, because:

1. The size of the coal used on the round kiln was greater and thus the voids for the passage of air through the firing opening were larger.
2. The ratio of the firing opening to the effective grate area, as shown in item 10 of Table I and hence the ratio of secondary air supply to combustible, was much larger for the dead bottom furnace than for the grate bar furnace.

The fresh charges of coal lay in the openings on the hub and it was evident from observation that a large part of the volatile content of the coal did not enter the kiln. Had it entered the kiln there would have been a higher content of combustible gases in the samples from above the fire-boxes, particularly immediately after firing.

The absence of combustible gases in this kiln was, therefore, owing to the fact that the combustion in the furnace was rapid because of a high ratio of secondary air to combustible and to the loss of volatile combustible matter outside the kiln.

The rate of combustion of the gases within the kiln itself was of the same order as in the rectangular kiln.

The readings taken in this kiln show the existence of a pressure greater than atmospheric near the top of the kiln.

Conclusions

This investigation showed that combustion of the gases arising from the fuel bed took place very rapidly in both types of kilns. The incandescent checker work of the setting furnished the previously noted requirements for rapid combustion of the gases, namely, thorough mixing, and high combustion chamber temperature. The hot surface of the ware also undoubtedly acted as a catalyst for the reactions.

In samples taken over a short period combustible gases occurred only in the absence of oxygen. Combustion of the gases took place almost immediately upon admission of secondary air to the gas stream and delayed combustion could, therefore, only be secured by delaying the admission of the secondary air. As there was a pressure greater than that of the air at the same level at all points in the upper part of the kilns, secondary air could be introduced here only by means of a forced draft system. The air could be introduced into the bottom and center of the kiln by natural draft through air ducts to the desired points.

Another method, applicable to the rectangular kiln, would be that of firing alternate ends of the kiln, one tightly closed to secure a large supply of combustible gases and the other open to provide an excess of air. The combustion of the gases would take place when the two gas streams met and thus the heat of the gases would be released closer to the ware at the center and bottom of the kiln. An obvious difficulty of this method, when the firing openings are closed by coal, would be to maintain the deficiency in air supply over a considerable period of time. If the coal burned down to admit enough air for complete combustion the gas temperature would rise very high and the ware near the fire-boxes would be over-burned.

This method has been tried on later burns at this plant. On the first trial the ends were over-burned but a higher temperature was secured in the bottom. By further work with the method they have reduced the coal consumption and have reduced the temperature difference between ends and center by more than 2 cones.

This method does not lend itself so well to the round kiln owing to the more uniform distribution of the fire-boxes around the periphery.

Although the gaseous combustion takes place so rapidly, the combustion of the carbon particles, as has been pointed out, is very slow and extends throughout the kiln and possibly through the flues and stack. These incandescent particles of soot, together with ash, are the flames observed in the setting and often at the top of the stack. The heat liberated by the combustion of the soot within the setting is probably inconsiderable compared to that which would result from the combustion of gases.

The incandescent particles, however, perform an important function in the distribution of the heat in the kiln. They are heated to incandescence by the heat of combustion at the fuel bed and carry this heat within the setting to deliver it to the ware by radiation. If this flame were absent, the ware in the interior of the setting would receive heat only by convection and by conduction from the hotter outer ware which is also receiving heat by radiation from the fuel beds. The transmission of heat by radiation varies as the fourth power of the absolute temperature, whereas transmission by convection and conduction varies as the first power of the temperature difference.

This is the value of the "long flame" coals and "long flame" conditions in a brick kiln or in any process requiring a uniform temperature where a large mass of the material to be heated is out of "sight" of the fuel bed.

To again sum up the results, it was found in the two types of refractory kilns investigated that:

1. Combustion of the gases from the fuel bed was complete within a short distance from the point of secondary air admission.
2. Combustion of the gases can be carried to the center and bottom of the kiln only by the admission of secondary air at the desired point. This may be done by means of forced draft or air ducts according to whether the pressure at the point is above or below that of the atmosphere, or by a method of alternate firing in the rectangular type of kiln.
3. The attainment of a uniform temperature throughout the kiln is, in general, a problem of the uniform distribution of the hot gases rather than one of gaseous combustion.

NOTE: Grateful acknowledgment is made of the assistance and suggestions of John Blizard, Fuel Engineer, and G. A. Bole, Superintendent of the Columbus Station of the Bureau of Mines, at whose suggestion and under whose direction the work was undertaken, of the valuable assistance of the members of the crew of the car "Holmes," and of the kind coöperation of the superintendents and workmen at the plants where the work was done.

STRENGTH, ABSORPTION AND FREEZING RESISTANCE OF HOLLOW BUILDING TILE[1]

By H. D. Foster

ABSTRACT

This paper describes the test methods and gives a summary of the compressive strength and absorption determinations of nearly 350 tests of tile selected from twenty-five representative sources. A preliminary report of the resistance to freezing and thawing of tile from seventeen representative sources is also given. The following conclusions were made: (*a*) The weight of tile per unit of solid material varies from 20 to 30%. (*b*) The weight per unit volume of material is closely related to the absorption and decreases as the absorption increases. (*c*) The strength of tile varies with the type of raw material used. (*d*) The unit strength based on gross area of an end construction tile tested on edge is 38% of that obtained when tested on end. (*e*) The relation between strength and absorption is not linear but a plotted curve shows increasing gain in strength with a decrease in absorption. (*f*) Color cannot be taken as indicative of strength. (*g*) The modulus of elasticity varies from 1,600,000 to 6,060,000 and is approximately directly proportional to the strength and inversely proportional to the absorption. (*h*) An absorption of 16% apparently marks a very definite line in the resistance of tile to freezing and thawing.

1. Introduction

Only a little information showing the physical properties of the various grades of hollow building tile has been made available and is insufficient for the intelligent formation of standard specifications and building code requirements. The industry, aware of this condition, has during the past few years coöperated with the Bureau of Standards in conducting a considerable amount of research work on its product primarily to obtain information on hollow tile as a fire retardant. Along with the fire tests, auxiliary tests are being made on representative tile to determine compressive strength, absorption and resistance to freezing, on the results of which this paper is a preliminary report. Papers dealing with the methods of procedure in making compressive strength and absorption determinations have been previously given before this SOCIETY.[2]

2. Scope of Tests

Hollow building tile is manufactured from a wide range of clay materials. These fall into the following general classes: (*a*) shales, (*b*) dense burning fire clays, (*c*) open burning fire clays, (*d*) surface clays.

Approximately 350 tiles from 25 representative sources, including 7 shales, 5 dense burning fire clays, 4 open burning fire clays, and 9 surface clays

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[1] Recd. Jan. 11, 1924. Presented at the Atlantic City Meeting, February, 1924. (Heavy Clay Products Division.)

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[2] H. D. Foster, "Capping for Compression Specimens," *Jour. Amer. Ceram. Soc.*, **6** [5], 623–9 (1923); "Effectiveness of Different Methods of Making Absorption Determinations," *Ibid.*, **5** [11], 788–97 (1922).

were tested in compression. Most of the compression tests were made with the tile in the position in which they are normally used. Some of the end construction tile were also tested on edge, a position in which they are sometimes used. The absorption of all tile broken in compression was determined. Stress-strain readings for the modulus of elasticity determinations were taken on 80 tile from 18 representative sources. Freezing tests are being made on pieces of 54 tile taken from 18 representative sources.

The sizes of the tile tested were those most commonly used in load-bearing construction, namely, 8 x 12 x 12 inches, 4 x 12 x 12 inches, 8 x 5 x 12 inches, Denison "H" and Interlocking. Information on the effect of size on strength can be obtained from a previous publication wherein the strengths of various sizes of tile, mostly of a fire clay origin, are given.[1]

3. General Test Procedure

(*a*) **Selecting, Weighing and Measuring Test Samples.**—Five or more tile representative of the variations in quality obtaining at each plant were selected for the tests. The dry weights of these tile were then determined. As the net horizontal sectional area of each tile when laid in the position in which it is to be tested is necessary as a basis for the computation of the increments of loading and the unit load, the exact size of the tile and the thickness of the shells and the webs were measured with calipers. From these measurements the net and gross sectional area and the volume of solid material in the unit were computed.

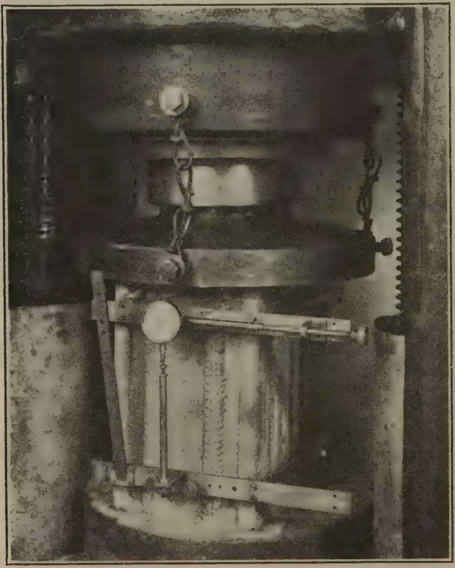

FIG. 1.

(*b*) **Details of Compression Tests.**—Previous to testing, the tile were capped to insure uniform bearing in the testing machine. After coating the bearing surfaces and adjacent parts with shellac to keep the tile from absorbing water from the plastic cap, they were capped with a mixture of one part of plaster of Paris and three parts of cement in the following manner: A quantity of the capping material mixed with enough water to give it a consistency such that it could be spread evenly on a glass plate which had been moderately coated with oil. One bearing surface of the tile was then set in this plastic material and while holding the tile so that with axis vertical it was fixed in position by the application of a single firm pressure. As soon as the cap had hardened sufficiently the tile was removed from the plate and the other end capped in the same manner. The caps were from $^1/_{16}$ to $^1/_8$ inch thick. No caps were patched, imperfect ones being removed and replaced with new ones. The caps were allowed to age from 5 to 7 days before the tile were tested.

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[1] Bureau of Standards, *Tech. Paper* **120**, "Tests of Hollow Building Tiles."

In testing, each tile was placed on the weighing table of the machine (Fig. 1) in such manner that its vertical axis coincided with a vertical line passing through the center of the movable head and through the center of the hemispherical bearing block. As the movable head was lowered the lower part of the bearing block was allowed to seat itself on the top bearing surface of the tile and the top part of the bearing block was slowly rotated as it came in contact with the movable head in order to secure even bearing. By carefully placing the tile in this manner no difficulty was experienced in consistently obtaining good breaks many of which showed very definitely the typical compression cone.

The tests were made in a 300,000-pound Riehlé testing machine, the actual breaking speed of the moving head being slightly less than 0.05 inch per minute. The load was applied continuously, readings of the compressometer being taken at loading increments of 500 pounds per square inch of net sectional area. The compressometer used (Fig. 1) consists essentially of a bottom yoke which is attached rigidly to the tile, a top yoke which is pivoted by two screws placed on the sides and opposite the vertical axis of the test specimen. The rear of this yoke is held a fixed distance from the bottom yoke. The front of this yoke is free to move downward with the deformation of the center of the tile, the movement with respect to the bottom yoke being measured with a dial gage. This measurement when multiplied by an instrument constant gives the average deformation of the test specimen.

Strain readings were taken in tests when the tile was tested with its cells vertical. The initial strain reading was not taken until a load of 100 pounds per square inch of net sectional area had been applied. Further readings were taken at loading increments of 500 pounds per square inch until failure was approached.

(*c*) **Details of Absorption Tests.**—Three pieces for absorption determinations were selected from each tile broken in compression. Two of the three pieces were taken from opposite shells and one from the center web. The pieces selected were free from cracks from the failure of the tile in compression and were of such size as to weigh not less than 225 grams or 8 ounces.

After the loose edges and rough particles were ground off, the pieces were dried to constant weight. They were then immersed in water and saturated by boiling for four hours and cooling to room temperature. After saturation the pieces were removed from the water and allowed to drain for not more than one minute. The superficial water was then removed with a damp cloth after which the pieces were weighed immediately.

The weight of the water absorbed multiplied by 100 and divided by the dry weight of the pieces gave the percentage absorption. While the absorption results in this paper are based on 4-hour boiling, it was found in a separate investigation[1] that only a small difference obtains with one-hour and four-hour boiling as applied to clay hollow tile.

(*d*) **Details of Freezing Tests.**—Three tiles, one hard-fired, one medium-fired and one soft-fired were selected from each of seventeen kinds of tile for the freezing tests. In order to avoid the presence of cracks in the specimens for freezing tests they were sawed from whole tile by means of a large stone saw. The absorption of these specimens was obtained as described above. The specimens were then placed in the freezing machine wherein they were alternately cooled and held for a few hours at a temperature below —10°C and thawed by a flow of tap water. Frequent inspections and weighings of the test specimens were made in order to determine the loss. Before each weighing all loosened pieces liable to be knocked off in ordinary usage were removed. Photographs showing the condition of the test specimens were made at intervals determined by the loss incurred.

4. Results and Discussion of Tests

(*a*) **Weight.**—The weight per unit volume of burned material in the tile tested, as shown in Table I, was found to vary from 0.060 to 0.082 pound per cubic inch, averaging 0.071 pound (from 103 to 141 pounds per cubic foot, averaging 123 pounds). These variations probably represent the range that can be expected as the tile tested were representative of the entire product of the industry. They do not, however, include the very porous material which has been made by the addition of large amounts of sawdust, this tile not being used for load bearing construction. The variations in weight depend upon the specific gravity of the clay as influenced by its mineral constituents and upon differences in porosity caused by differences in the fineness of grinding of the raw material, by non-uniformity in mixing the materials, by differences in pressure to which the clay is subjected while being molded and by differences in burning temperatures. As the variation in specific gravity is small, a fairly definite relation should be found between the absorption and the unit weight. This relation is shown graphically in Fig. 2. It is suggestive of a short way of approximating the absorption of tile.

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[1] "Effectiveness of Different Methods of Making Absorption Determinations," *loc. cit.*

(*b*) **Compression and Absorption Tests.**—A summary of the results of the compression and absorption tests, including the size and type of tile, the position in which tested, the sectional area, the maximum load sustained, the range and average unit load, the range and average percentage absorption and the modulus of elasticity, are given in Table I. The results are arranged in order of the strengths of the tile as based on their net sectional area. This gives them a rank in strengths as follows: shales, dense burning fire clays, open burning fire clays, and surface clays. From this table it can be seen that all of the shale and dense burning fire clay tiles that were tested could be classed as hard, that the open burning fire clay tiles and some surface clay tiles would be classed as medium, and that many surface clay tiles would be classed as soft. These statements do not hold, however, unless the tile is well burned.

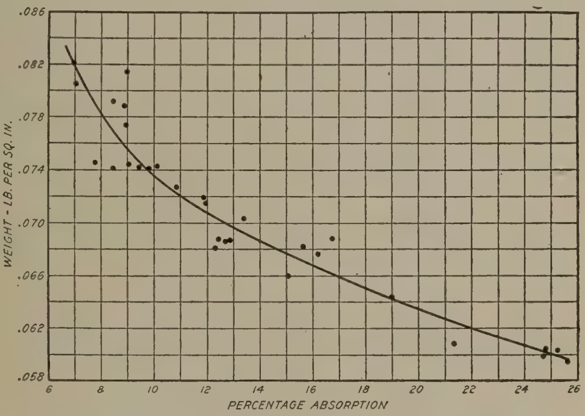

FIG. 2.—Relation between unit weight of constituent material in tile and absorption.

It is evident that there is a relation, as shown in Fig. 3, between absorption and strength, but this relation cannot be definitely fixed as applying to tile in general. A more definite relation can be derived and made to apply to the product from a given source of material.

It was found in general that the modulus of elasticity of the tile was nearly constant until failure. This is especially true with the denser burned tiles, as failure always occurred suddenly, while with the more porous tiles the modulus of elasticity gradually decreased as the maximum load was approached. In general it was found that the higher the modulus the higher the compressive strength. The modulus of elasticity varies inversely with the absorption as shown in Fig. 4. A similar but direct relation exists between the modulus of elasticity and the strength.

All kinds of end construction tile were also tested on edge, the strength of the tile when tested on edge being given in the table immediately following the strength of that same kind of tile when tested on end. It is shown that the strength of the tile when tested on edge is from 33 to 99%

as strong, based on net sectional area, as when tested on end. However, as the area in compression when the tile is laid on edge is on the average only 60% of that when it is laid on end, the actual strength of the unit on edge is approximately 20 to 60% of the strength on end. This difference can be attributed to the design of the tile and to the orientation of the lamination planes and clay particles during the flow of the plastic clay material through the die. In end construction tile these planes are always parallel to the direction of application of the load and have little effect on the strength, while with side construction tile they are always perpendicular to the direction of application of the load and appreciably affect the strength. This is evidenced by the Kentucky shale which has no laminations and which loses very little strength on the net sectional area when turned on edge, and by the New Jersey surface clay where laminations are present and which loses a large amount of strength when turned on edge. It must be appreciated, however, that this conclusion is not based on the results of tests of tiles designed for side construction whose efficiency in the masonry wall is probably greater than that of end construction laid on edge.

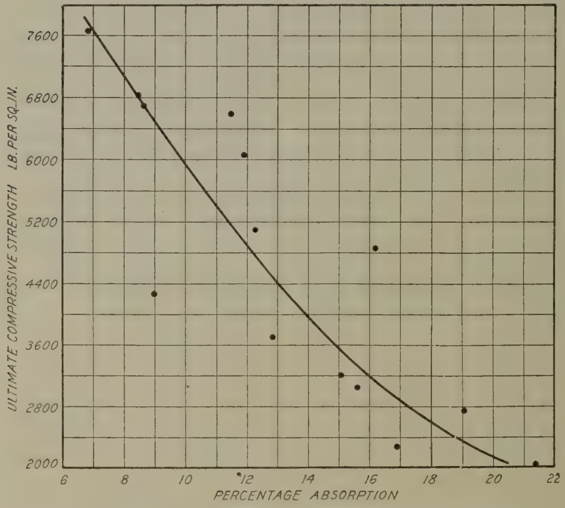

FIG. 3.—Relation between strength and absorption.

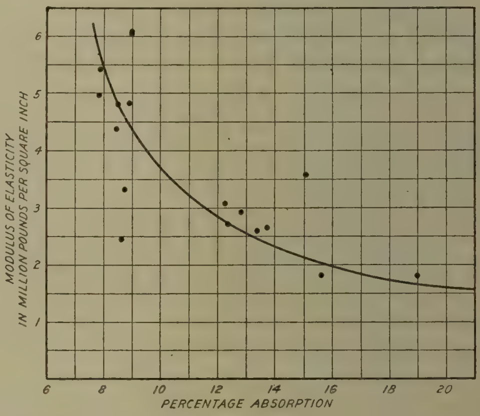

FIG. 4.—Relation between modulus of elasticity and absorption.

Attention should be called to the fact that there is no relation between strength and color or between absorption and color that can be used for all tile because of the various kinds of clay used in the industry.

TABLE I

SUMMARY OF RESULTS OF COMPRESSION AND ABSORPTION TESTS

Laboratory identification	Kind of clay	Source	No. of tests	Nominal size, inches	No. of cells	Position in which tested	Area under compression, sq. in.		Net volume, cu. in.	Weight		Maximum load, pounds	Unit strength				Absorption, per cent		Modulus of elasticity in million pounds per. sq. in.
							Gross	Net		Total	Per cu. in.		Lbs./sq. in. of gross area Range	Lbs./sq. in. of gross area Average	Lbs./sq. in. of net area Range	Lbs./sq. in. of net area Average	Range	Average	
A	Shale	Indiana	4	8x12x12	4	End	96.10	30.04	375.84	27.76	.0741	144330	1177 to 1804	1509	3591 to 5768	4838	6.6 to 12.4	8.44	4.354
	Shale	Indiana	3	8x12x12	4	Edge	96.50	17.93	....	...	...	47300	393 to 557	490	2085 to 3032	2643	6.0 to 12.3	7.52	.....
G	50% fire clay 50% shale	Alabama	5	8x12x12	4	End	98.44	36.65	424.51	32.71	.0744	157793	1204 to 2203	1606	3177 to 6070	4327	6.9 to 11.1	8.91	4.814
	50% fire clay 50% shale	Alabama	4	8x12x12	4	Edge	93.99	20.47	....	...	...	91649	866 to 1155	975	3896 to 5427	4483	8.6 to 9.8	9.36	.....
F	Fire clay containing 15% shale	Ohio	5	8x12x12	4	End	100.55	34.44	414.14	28.41	.0688	152906	1082 to 1968	1520	3000 to 5918	4454	10.9 to 13.7	12.39	2.731
	Fire clay containing 15% shale	Ohio	3	8x12x12	4	Edge	99.90	21.45	....	...	...	31392	289 to 360	314	1278 to 1700	1468	12.1 to 13.5	12.48	.....
O	High lime surface clay	Illinois	5	8x12x12	4	End	94.80	39.70	479.83	28.93	.0605	91606	680 to 1293	978	1597 to 3081	2304	22.7 to 25.8	24.85	1.620
	High lime surface clay	Illinois	5	8x12x12	4	Edge	96.33	26.15	....	28.89	...	40681	308 to 687	424	1155 to 2476	1554	22.7 to 25.6	24.07	.....
C	Shale	Iowa	3	8x12x12	6	End	93.40	29.63	350.78	28.54	.0814	127087	1275 to 1476	1362	4043 to 4570	4288	7.7 to 11.0	8.99	6.059
	Shale	Iowa	3	8x12x12	6	Edge	95.62	18.99	....	...	...	34580	326 to 397	361	1612 to 2034	1825	8.1 to 12.5	9.71	.....
D	Shale	Kentucky	5	8x12x12	6	End	91.92	38.16	448.04	35.49	.0792	260191	1971 to 3453	2826	4697 to 8230	6821	6.4 to 10.9	8.47	4.826
	Shale	Kentucky	5	8x12x12	6	Edge	93.29	21.77	....	...	...	145011	1260 to 1932	1557	5431 to 8224	6667	7.1 to 10.6	8.56	.....
	Shale	Kentucky	5	8x12x12	6	End	93.06	38.15	446.05	36.61	.0821	293057	2726 to 3520	3150	6737 to 8614	7683	5.8 to 7.5	6.89	.....
L	Dense burning fire clay	Ohio	5	8x12x12	6	End	98.31	40.99	482.69	34.70	.0715	250325	1592 to 3008	2546	3834 to 7127	6118	10.8 to 15.0	11.92	.....
	Dense burning fire clay	Ohio	5	8x12x12	6	Edge	96.35	22.00	493.61	35.52	.0719	95155	852 to 1092	989	3777 to 4808	4325	10.6 to 12.5	11.89	.....
	Dense burning fire clay	Ohio	5	8x12x12	6	End	96.33	42.26	....	35.26	...	278836	2610 to 3114	2897	5949 to 7099	6598	10.5 to 12.4	11.47	.....
	Dense burning fire clay	Ohio	5	8x12x12	6	Edge	96.02	21.43	....	35.14	...	93976	848 to 1157	978	3797 to 5185	4385	9.6 to 14.0	11.69	.....
M	Dense burning fire clay	Ohio	5	8x12x12	6	End	99.11	39.74	....	...	...	265868	2451 to 2975	2681	6113 to 7418	6691	7.6 to 11.0	8.65	2.426
	Dense burning fire clay	Ohio	5	8x12x12	6	Edge	97.43	18.55	....	32.30	...	75619	599 to 996	776	3145 to 5230	4076	5.7 to 10.4	8.12	.....
N	Open burning fire clay	New Jersey	5	8x12x12	6	End	91.76	38.26	452.30	30.77	.0681	206040	1783 to 2723	2250	4438 to 6565	5103	8.7 to 14.5	12.29	3.080
	Open burning fire clay	New Jersey	5	8x12x12	6	Edge	91.42	19.59	....	30.95	...	53186	461 to 680	581	2075 to 3298	2722	8.7 to 13.0	11.14	.....
P	Open burning fire clay	New Jersey	5	8x12x12	6	End	92.85	42.01	509.27	34.98	.0687	155160	1228 to 2017	1675	2713 to 4461	3704	11.0 to 15.7	12.85	2.920
	Open burning fire clay	New Jersey	5	8x12x12	6	Edge	94.18	21.76	....	35.86	...	51251	470 to 611	544	1981 to 2625	2359	12.2 to 15.6	13.62	.....
H	Open burning fire clay	Texas	5	8x12x12	6	End	90.42	41.84	495.99	33.81	.0682	127094	1091 to 1568	1408	2350 to 3334	3042	14.5 to 17.2	15.61	1.818
	Open burning fire clay	Texas	3	8x12x12	6	Edge	92.99	26.29	....	...	...	31330	312 to 368	336	1086 to 1313	1192	15.2 to 17.0	15.81	.....
K	Surface clay	New Jersey	5	8x12x12	6	End	91.88	43.50	515.74	33.60	.0660	138771	1369 to 2036	1508	3033 to 4342	3213	7.8 to 19.2	15.07	3.595
	Surface clay	New Jersey	3	8x12x12	6	Edge	91.64	27.16	....	...	...	32516	275 to 441	355	966 to 1439	1193	11.4 to 17.4	13.57	.....
Y	Surface clay	New Jersey	5	8x12x12	6	End	100.93	41.58	499.72	33.85	.0677	202777	1806 to 2237	1900	4367 to 5360	4872	15.0 to 17.6	16.20	.....
	Surface clay	New Jersey	5	8x12x12	6	Edge	98.04	19.90	501.83	33.82	.0668	50476	386 to 644	516	1983 to 3286	2538	16.1 to 17.3	16.74	.....
Q	Surface clay	Massachusetts	5	8x12x12	6	End	92.91	37.45	447.67	32.40	.0741	237729	1894 to 3871	2639	4487 to 11075	6644	2.4 to 15.3	9.79	4.418
	Surface clay	Massachusetts	4	8x12x12	6	Edge	99.89	21.65	....	33.74	...	49329	407 to 543	493	1806 to 2686	2296	16.0 to 17.7	16.88	.....
J	Surface clay	New York	5	8x12x12	6	End	98.28	52.53	536.02	40.86	.0644	144504	1296 to 1667	1473	2347 to 3176	2761	16.2 to 20.8	19.02	1.825
	Surface clay	New York	5	8x12x12	6	Edge	100.40	32.38	....	41.10	...	71481	525 to 889	710	1523 to 2974	2253	14.7 to 23.1	19.43	.....
	Surface clay	New York	5	8x12x12	9	End	89.37	46.59	566.99	34.51	.0609	93863	584 to 1437	1050	1104 to 2743	2019	16.8 to 24.4	21.39	.....
D	Shale	Kentucky	5	4x12x12	3	End	45.48	21.24	246.25	19.83	.0805	241181	4719 to 5645	5304	10175 to 12195	11349	6.4 to 7.5	7.02	.....
	Shale	Kentucky	5	4x12x12	3	Edge	46.19	13.24	254.43	20.08	.0789	121343	2237 to 3068	2630	7858 to 10578	9216	7.2 to 9.6	8.87	.....
L	Dense burning fire clay	Ohio	5	4x12x12	3	End	46.73	20.80	245.88	18.23	.0742	189786	3311 to 4572	4060	7452 to 10610	9197	8.2 to 11.0	9.42	.....
	Dense burning fire clay	Ohio	5	4x12x12	3	Edge	46.64	12.15	244.05	18.14	.0744	86713	1527 to 2296	1861	6032 to 8812	7141	7.6 to 10.3	9.01	.....
J	High lime surface clay	New York	5	4x12x12	3	End	47.80	23.01	282.53	16.79	.0595	61595	940 to 1515	1291	1922 to 3227	2689	25.0 to 26.5	25.64	.....
	High lime surface clay	New York	5	4x12x12	3	Edge	48.47	14.97	....	16.69	...	28876	512 to 744	596	1631 to 2394	1932	24.8 to 27.0	26.11	.....
	High lime surface clay	New York	5	4x12x12	3	End	47.65	25.25	308.47	18.46	.0599	78584	1106 to 1989	1654	2323 to 3720	3102	23.6 to 25.4	24.77	.....
	High lime surface clay	New York	5	4x12x12	3	Edge	48.70	17.69	....	18.54	...	39311	493 to 1241	807	1354 to 3500	2229	23.4 to 25.5	24.53	.....
B	Shale	Iowa	3	8x5x12	3	Side	94.32	21.18	....	15.04	...	67987	687 to 751	721	2920 to 3489	3227	1.4 to 18.1	11.92	4.994
C	Shale	Iowa	5	8x5x12	3	Side	99.51	26.34	....	16.03	...	90902	839 to 1020	914	3175 to 3943	3457	9.0 to 14.4	10.50	6.059
D	Shale	Kentucky	5	8x5x12	2	Side	93.95	22.16	195.79	14.54	.0743	117140	1292 to 1617	1376	5348 to 6680	5730	8.6 to 10.9	10.09	.....
E	Shale	Kansas	5	8x5x12	2	Side	98.21	23.04	215.13	15.29	.0703	67747	572 to 877	690	2388 to 4048	2967	11.1 to 14.8	13.39	2.657
L	Dense burning fire clay	Ohio	2	8x5x12	2	Side	97.12	22.36	198.88	14.84	.0746	132710	1028 to 1702	1365	4608 to 7165	5886	6.4 to 8.6	7.77	5.443
M	Dense burning fire clay	Ohio	3	8x5x12	2	Side	98.30	21.48	....	16.09	...	71658	607 to 950	731	2831 to 4266	3336	6.8 to 10.3	8.74	3.325
R	50% shale 50% surface clay	Ohio	5	8x5x12	2	Side	94.07	20.32	184.65	13.42	.0727	119712	1154 to 1451	1273	5368 to 6705	5885	10.2 to 12.0	10.83	.....
HO	Surface clay	Indiana	11	8x5x12	3	Side	97.30	32.33	....	15.05	...	75065	600 to 1055	767	1798 to 3083	2309	24.1 to 26.1	25.11	.....
ST	Surface clay	Georgia	12	8x5x12	3	Side	95.13	26.75	....	14.79	...	90691	730 to 1482	1000	2438 to 5042	3372	12.8 to 16.8	14.40	.....
BA	Dense burning fire clay	Ohio	25	8x5x12	2	Side	92.87	22.61	....	14.92	...	109499	864 to 1622	1182	3574 to 6635	4855	6.9 to 16.3	11.55	.....
MC	Shale	Iowa	5	Denison H No. 47	...	Side	95.73	27.44	446.86	30.67	.0686	61413	408 to 862	644	1432 to 2985	2239	10.5 to 15.4	12.66	.....
L	Dense burning fire clay	Ohio	10	Denison H No. 47	...	Side	95.85	27.07	....	32.55	...	137868	989 to 1741	1439	3539 to 6273	5113	8.9 to 12.4	10.54	.....
PB	Shale	Kentucky	10	Interlocking	...	Side	93.28	23.31	....	15.12	...	114984	839 to 1527	1259	3237 to 6203	4954	6.8 to 15.3	11.38	.....
CP	Fire clay	Indiana	10	Interlocking	...	Side	98.73	26.06	....	17.81	...	114791	864 to 1580	1156	3384 to 5680	4407	4.1 to 10.2	6.41	.....
FR	Open burning fire clay	Texas	8	Interlocking	...	Side	95.55	35.24	....	17.75	...	136100	1278 to 1638	1425	3505 to 4296	3861	9.0 to 13.1	10.62	.....
FR	Surface clay	Texas	10	Interlocking	...	Side	98.72	29.62	....	18.31	...	93116	835 to 1134	942	2770 to 3742	3141	9.7 to 15.3	12.95	.....
Y	Surface clay	New Jersey	10	Interlocking	...	Side	95.08	23.91	....	14.74	...	53253	446 to 672	559	1668 to 2692	2231	11.6 to 15.3	13.45	.....
	Surface clay	New Jersey	10	Interlocking	...	Side	90.95	22.34	....	14.67	...	62774	535 to 928	691	2108 to 3801	2819	7.4 to 9.7	8.62	.....

There may be, however, a fairly definite relation that can be applied to the products from each source.

No definite relation between the weight of the tile unit and the strength can be derived from these tests, although the trend of results indicates a general increase of gross area strength with increase in weight. Although tile of varying weights were tested, they were from different sources wherein the variation in clay was so great that this relation was more or less concealed. With one exception, all tile from each source were in general of the same weight. In the one case two lots of tile were submitted. In the second lot the weight of the unit was increased 18.4% and the strength was increased 41.3%. A part of this increase in strength was due to a 2.4% reduction in absorption.

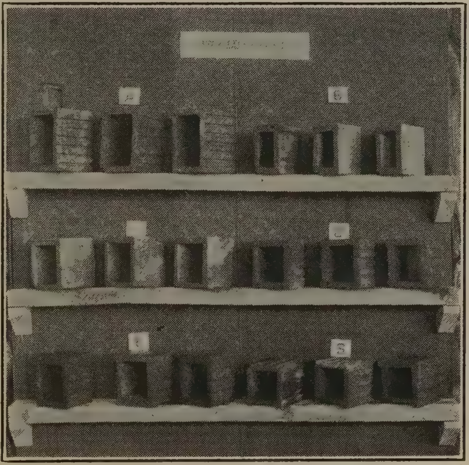

FIG. 5.—Condition of shale tile after 100 alternate freezings and thawings.

(*c*) **Freezing Tests.**—The work on freezing, though not complete,

TABLE II

RESULTS OF FREEZING TESTS

Laboratory identification	Kind of clay	Percentage absorption	Percentage loss after 90 freezings
A	Shale	10.5	1.6
B	Shale	5.5	0.0
C	Shale	7.3	0.0
D	Shale	9.9	0.1
E	Shale	12.6	0.2
S	Shale	6.9	0.1
F	Fire clay	9.3	0.0
H	Fire clay	12.0	1.3
L	Fire clay	6.8	0.0
M	Fire clay	6.5	0.0
N	Fire clay	8.7	0.0
P	Fire clay	8.8	0.0
J	Surface clay	22.1	3.7
K	Surface clay	13.3	0.1
O	Surface clay	21.8	13.1
Q	Surface clay	6.4	0.4
R	Surface clay	10.3	0.2

TABLE III

CHEMICAL ANALYSIS OF HOLLOW BUILDING TILE CLAYS

Laboratory identification	Kind of clay	Source	SiO_2	Total iron as Fe_2O_3	Al_2O_3	Mn_3O_4	P_2O_5	CaO	MgO	Na_2O	K_2O	SO_3	CO_2	Loss on ignition[1]	Total flux
A	Shale	Indiana	50.90	10.20	18.53	0.15	1.80	2.23	2.07	0.41	3.03	0.18	4.30	9.98	19.89
B	Shale	Iowa	48.92	4.30	17.97	trace	0.09	6.27	4.09	0.09	4.10	0.93	8.71	12.68	18.94
C	Shale	Iowa	31.74	9.90	1.91	0.09	0.26	17.22	10.19	0.27	1.18	0.20	23.90	26.52	39.11
D	Shale	Kentucky	57.68	8.10	18.00	0.06	1.54	1.01	2.21	0.83	4.07	0.65	1.04	6.16	17.82
E	Shale	Kansas	55.66	6.00	16.40	trace	1.36	0.46	3.53	0.93	2.59	0.23	0.29	12.34	14.87
F	Fire clay	Ohio	57.68	1.70	27.53	trace	0.13	0.31	0.80	0.33	1.67	1.10	4.28	9.58	4.94
G	Shale	Alabama	62.12	5.40	19.95	trace	1.27	0.18	1.34	0.47	2.97	0.24	0.00	6.38	11.63
H	Fire clay	Texas	63.20	0.20	26.43	0.07	trace	0.20	0.36	0.13	0.30	0.34	0.03	9.14	1.26
J	Surface clay	New York	57.66	5.75	16.04	0.04	0.29	6.46	2.79	1.35	2.87	1.15	0.85	5.16	19.55
K	Surface clay	New Jersey	57.45	7.25	19.36	trace	0.14	0.30	1.12	0.60	1.57	3.68	0.50	11.15	10.98
L	Fire clay	Ohio	55.32	4.20	24.97	trace	0.33	0.39	0.75	0.59	2.08	3.41	0.39	10.46	8.34
M	Fire clay	Ohio	61.40	1.50	26.60	trace	trace	0.55	0.37	0.60	0.90	1.13	0.00	8.05	3.92
N	Fire clay	New York	67.70	3.55	18.48	trace	0.37	0.20	0.52	0.50	1.75	1.15	0.20	6.65	6.89
O	Surface clay	Illinois	49.74	0.70	17.55	0.05	0.34	8.48	4.85	0.65	3.38	0.39	9.55	13.88	18.45
P	Fire clay	New Jersey	61.45	2.15	22.80	trace	trace	0.35	0.30	0.34	2.14	2.24	0.02	9.35	5.28
Q	Surface clay	Mass.	57.65	5.05	21.83	0.09	0.48	1.45	2.59	2.12	3.88	0.15	0.05	4.03	15.66

Organic material detected in all samples, appreciable amounts being present in samples F, G, H, J, K, L, M, N and P.

[1] This figure represents total loss on ignition at the temperature of the blast and is the algebraic sum of various changes including loss of CO_2. (See W. F. Hillebrand, U. S. Geol. Surv., *Bull.* **700,** 231, and J. W. Mellor, "Treatise on Quantitative Inorganic Analysis," pages 157–159.) The results for samples K, L, M, N and P are apparently too high, probably owing to the reduction of sulphate to sulphide by the organic matter present.

has been carried far enough to indicate what tiles are liable to fail when subjected to freezing conditions. The detailed results of the first 90 alternate freezings and thawings are shown in Table II. The condition of the specimens after 100 freezings is shown in Figs. 5, 6 and 7. It will be noted from this table and the figures that the tile having an absorption over 16% were not able to withstand 100 alternate freezings and thawings without decided effects. The tile having the highest absorption suffered the greatest loss in freezing. From the photographs it can also be seen that tile with laminations are more likely to show effects in the freezing tests than tile of uniform structure.

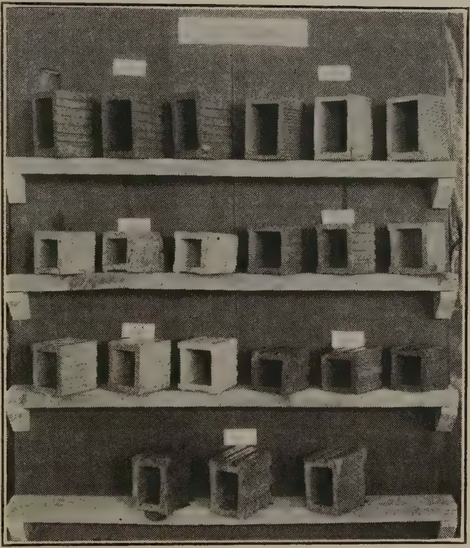

Fig. 6.—Condition of fire clay tile after 100 alternate freezings and thawings.

(*d*) **Miscellaneous Determinations.**—The chemical composition and the fusion point of the clays have been determined and are given in Tables III and IV. These determinations were made so their relation to fire resistance might be studied. No attempt has been made to derive their relation to the strength, absorption and freezing resistance, but they are given here as an aid in defining the clay materials from which the tile tested were made.

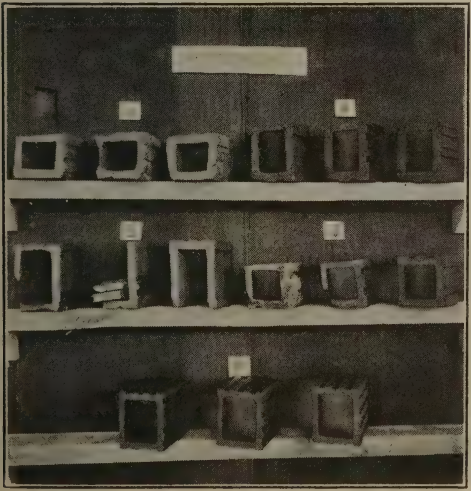

Fig. 7.—Condition of surface clay tile after 100 alternate freezings and thawings.

5. Conclusions

The following conclusions, drawn from the tests collated in this paper, are based directly on the results obtained, and have a fairly wide application owing to the range in tile tested. In drawing independent conclusions, however, it must be remembered that there are great variations because of the many classes and grades of clay used in hollow tile manufacture, and those results obtained from tile made from the same grade and type of clay in question should be used.

TABLE IV

FUSION POINTS OF HOLLOW BUILDING TILE CLAYS

Laboratory identification	Kind of clay	Source	Fusion point, degrees Centigrade
A	Shale	Indiana	1100
B	Shale	Iowa	1140
C	Shale	Iowa	1145
D	Shale	Kentucky	1180
E	Shale	Kansas	1240
F	Fire clay	Ohio	1390
G	Shale	Alabama	1325
H	Fire clay	Texas	? (Cone 19)
J	Surface clay	New York	1170
K	Surface clay	New Jersey	1335
L	Fire clay	Ohio	1350
M	Fire clay	Ohio	? (Cone 20)
N	Fire clay	New York	1390
O	Surface clay	Illinois	1130
P	Fire clay	New Jersey	? (Cone 19)
Q	Surface clay	Massachusetts	1330

In obtaining these fusion points the furnace was heated to 1000°C in one hour. After the first hour the temperature was increased at the rate of 50°C per hour until the fusion point was reached. A platinum, platinum-rhodium thermocouple was used, the end of which was placed not more than three-eighths inch from the tip of the test cone. Each determination was checked two or more times. The fusion points of three clays, H, M, and P, were not accurately determined but were compared with Orton pyrometric cones.

1. The weight of tile per unit volume of solid material varies from 20 to 30% with the change in specific gravity of the clay and the details of manufacture.

2. The weight per unit volume of material is closely related to the absorption and decreases as the absorption increases.

3. The strength of tile, if well burned, varies with the type of raw material used; shales, dense burning fire clays, open burning fire clays, and surface clays generally giving strengths in the order named, although not without marked exceptions.

4. The unit strength on net area of end construction tile when tested on edge is, as based on average values, 65% of that obtained when the tile is tested on end, or as based on gross area the strength when tested on edge is 38% of that obtained when tested on end. This is offset to some extent by the fact that the efficiency of the unit in the wall is greater when laid on edge than when laid on end.

5. With well burned tile, there is a fairly definite relation between absorption and strength. This relation is not linear, the curve shows an increasing gain in strength with a decrease in absorption.

6. Color cannot be taken as indicative of strength because of the many kinds of clay used in the tile industry.

7. The modulus of elasticity varies from 1,600,000 to 6,060,000 pounds per square inch approximately directly with the strength and inversely with the absorption.

8. An absorption of 16%, apparently marks a very definite line in the resistance to freezing and thawing. Tile of lower absorption showed little or no effects from 100 freezings and thawings while tile of higher absorptions incurred loss from the loosening and falling away of small spalls and were appreciably weakened.

Acknowledgments

The work of which this paper forms a part is conducted at the U. S. Bureau of Standards in coöperation with the Hollow Building Tile Association. The writer wishes to express his appreciation to the manufacturers who, through their Association, have furnished material for tests, and to S. H. Ingberg, Chief of the Fire Resistance Section, and others who gave valuable help in making the determinations and preparing the report.

Bureau of Standards
Washington, D. C.

HOW TO GET RID OF SCUM ON A TANK MELTING FLINT BOTTLE GLASS[1]

By J. William Gayner

Scum which is commonly known to the layman in glass houses is quite a bothersome affair as it curtails the melting tonnage of the tank and also has a tendency to seed and streak the glass.

I would not undertake explaining what makes scum, as I do not know. I have heard this question discussed by many able glass men and they vary in opinion. One claims it comes from the soda, another from the lime, and another from lowering the temperature of the furnace on Saturday and Sunday blocks. In general practice these few things, which I will enumerate, help to get rid of scum.

Old Lime.—It is oftentimes the practice to let the fresh lime be dumped in the bin on top of the old lime, consequently the old lime is losing its strength, and then when the lime gets low, they will go back and get this old lime in the back of the bin which has been laying there for a long time. I have made a practice of using the old lime before we start using the new lime.

Old Soda.—The same thing holds good in regard to soda. By having twin bins or shoveling the old shipment forward, before the new shipment is unloaded on the old, will keep these materials in better condition.

Irregular Furnace Operation.—I think the greatest cause is the irregular running of the furnace, allowing the furnace to get cold Saturday nights and Sunday, and then bringing it up quickly so as to be ready for work on Monday.

I have tried to avoid these conditions, but even so I have scum on the tank. A simple method, which I am going to try to explain, has been a big help to me for a number of years.

I have a couple of men Sunday morning open the skimming hole just before the bridge in the melting pot. The furnace will be lower in temperature, so they can skim off all the dross, rough matter and scum. By so doing each Sunday morning, we keep rid of the scum. I realize that the bridges in some furnaces are so constructed that it is impossible to have the skimming hole so arranged as to do what I have described, but my practice is always to push the bridge away from the last port so as to have room for the skimming hole.

Lynchburg, Virginia

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[1] Presented at the Atlantic City Meeting, February, 1924. (Glass Division.)

REFRACTORY CLAYS AND SHALES OF INDIANA[1]

By W. N. Logan[2]

The refractory ceramic materials of Indiana are obtained from kaolin (halloysite or Indianaite), from fire clays or under clays, and from shales. The halloysite deposits occur largely at the contact between the Pottsville (Mansfield) sandstone and aluminous shales of the Chester group of the Mississippian, but minor deposits also occur at the contact of Chester shales and sandstones.

The fire clays are found in the Coal Measures or Pennsylvanian rocks. They are generally present beneath beds of coal but sometimes they are found unassociated with coals.

Some of the shales of the Chester group contain a high per cent of aluminium, only a small per cent of fluxing impurities, and, as a result, exhibit a moderately high degree of refractoriness.

Preparatory treatment of these last two sources of Indiana refractories have, in some samples at least, increased the degree of refractoriness. For example, weathering and washing of some of the under clays and some of the shales have increased their refractoriness.

Geographical Distribution.—All of these refractory substances are found in the western and in the southwestern portions of Indiana. The largest kaolin deposits have been found in Lawrence County but other deposits occur in Owen, Monroe, Greene, Martin and Orange counties.

The under clays are found in twenty-six counties of the state. They occur in the counties mentioned below and in the vicinity lying west of these counties. The Chester shales outcrop east of the outcrop of the Coal Measures in Perry, Crawford, Orange, Martin, Lawrence, Monroe, Greene, Owen and Putnam counties.

To the beds of white Indiana kaolin Cox gave the name "Indianaite." The principal part of the deposit is halloysite though allophane and gibbsite are also present.

Physical Properties.—The pure halloysite is a white substance of porcelain-like appearance. When first taken from the deposit it often exhibits a pale sea-green color and is semi-translucent. After exposure to the air, it loses its green color and becomes opaque-white. The large fragments of kaolin break up into irregular particles which do not pass readily into the plastic state but even when reduced to a fine condition possess only a moderate degree of plasticity.

The kaolin of the deposit is porous and when dry contains much air. The per cent of absorption of water by weight varies from 6.6 to 13.

The kaolin fragments contain plane surfaces which correspond to cleav-

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[1] Recd. Dec. 14, 1923. Presented at the Atlantic City Meeting, February, 1924. (Refractories Division.)

[2] State Geologist.

age planes but there is no regular cleavage system. The fracture in some fragments is distinctly conchoidal. The average hardness is about 2.5. However, there is a soft putty-like variety which hardens on exposure to the air. The specific gravity varies from 2 to 2.33.

Under the microscope the white kaolin is seen to be composed of minute globular granules which are often arranged in a dendritic form. These granules are translucent in appearance and have about the same index of refraction as balsam. The field sometimes contains larger structures composed of concentric rings of granules.

Chemical Properties.—The theoretical composition of halloysite is: silica, 43.5, alumina, 36.9, and water 19.6. Allophane has the composition: silica 20, alumina 40, and water 20.

The average of three analyses of the Indiana halloysite exhibits silica 39.08 parts, alumina 36.58, and water 23.33. The average impurities are only .35 parts.

The fusion point of the white kaolin ranges from 3300°F to 3400°F. The presence of iron, manganese and other elements in the stained kaolin reduces the fusion point.

Under Clays (Fire Clays)

The so-called "fire clays" of Indiana are associated with the coal-bearing rocks of the Pennsylvanian Period. There are about thirty-five beds of coal in the state and there are fire clays associated with the larger number of these. In addition there are some workable beds of fire clay not associated with coal. The clays underlying the following coals have been used extensively for ceramic purposes; Upper Block, Minshall, III, IIIa, and V. The under clays of other coals have been used less extensively.

Physical Properties.—The fire clays have an excellent degree of plasticity, are fine of grain, and are free from concretions or particles which are likely to cause imperfections in ceramic wares. They are grey in color, imperfectly laminated, and have a smooth, soap-like feel. They are often irregularly jointed, and slicken-sided surfaces are often present. At high temperatures they burn to a grey color, and the ware is generally free from cracks or crazes.

Analysis of Minshall Clay

	Per cent		Per cent
Loss on ignition	10.64	Iron oxide	1.92
Magnesium oxide	0.00	Silicon dioxide	58.90
Calcium oxide	0.76	Sulphur trioxide	1.31
Titanium oxide	1.40	Potassium oxide	0.48
Aluminium oxide	25.04	Sodium oxide	0.18
Total			100.63

Chemical Composition.—The chemical composition of the fire clays is variable. Variations occur as between beds and in individual beds. The per cent of alumina is usually between 20 and 25; the silica between 58 and 65; the fluxes from 3 to 4; and loss on ignition from 7 to 10. The table gives the analysis of a fire clay from beneath the Minshall coal.

Uses.—Fire brick have been manufactured from the under clays in a number of plants in Indiana. The brick were used largely for lining kilns and fire boxes, locally. The Simpson Brick Company located near Carbon have been manufacturing fire brick for many years. The brick are made from a mixture of the clay underlying Upper Block Coal and ganister. Both materials are obtained at the plant as the ganister occurs above the coal. The brick are placed upon the market. Other fire clay producing concerns in Indiana have sold clay which has been used elsewhere in the manufacture of refractories.

The writer has experimented with mixtures of Indiana under clays and halloysite, and has found that a very satisfactory high-grade refractory may thus be obtained. The fusion point of such mixtures varies from 3000°F to above 3300°F.

During a portion of the world war period a St. Louis firm manufactured a refractory called "Malinite." The material consisted of a mixture of Indiana halloysite and fire clay. Three samples of the Malinite were tested by R. W. Hunt and Company of Chicago as follows:

Three samples of Malinite refractories were selected, one white, one mottled and one brown. Portions of these brick were cut out and shaped into cones and mounted into a pat of Malinite, together with pyrometric cones numbered 30, 32, 34, 35, 36, 37, 38 and 39. After drying, the pat holding the pyrometric cones and test pieces was placed in an electric furnace of Hoskins manufacture, the current turned on and heating continued until the melting of cone 39.

The tests were started about 2:30 P.M. the same date. The atmosphere of the surface was reducing. The tests were conducted in the presence of J. H. Campbell, A. Malinovsky and W. W. Ittner. On August 22nd, the pat was taken from the furnace and the specimen of brick examined. There was no indication of fusion on the three samples tested. The temperature reached was 3542°F or better.

Load Tests under Heat

Full specimens of brick were placed in a furnace and heated up to 1350°C, about 2500°F in a period of $4^1/_2$ hours, and held at that temperature for $1^1/_2$ hours. Specimens were allowed to cool in the furnace over night. As tested the brick was set on end and a load of 25 pounds per square inch applied during the heating and cooling, as provided by specification of the American Society of Testing Materials C 16–17 T.

Description of sample	Mottled	Brown
Dimensions under compression	2.50 in. x 4.56 in.	2.55 in. x 4.50 in.
Height as tested	9.35 in.	9.43 in.
Area under compression	11.40 sq. in.	11.47 sq. in.
Total load applied	285 lbs.	287 lbs.
Load per square inch	25 lbs.	25 lbs.
Height after test	9.34 in.	9.34 in.
Per cent contraction	11/100	None

Neither sample showed signs of checking after the above test.

Cold Crushing Test

Description of sample	Mottled		Brown	
Test number	1	2	3	4
Specimen tested	On end	Flat	On end	Flat
Dimensions under compression	2.56″ x 4.66″	9.37″ x 4.54″	2.45″ x 4.59″	9.39″ x 4.54″
Area under compression	11.93 sq. in.	42.54 sq. in.	11.25 sq. in.	42.63 sq. in.
Height as tested	9.42 in.	2.49 in.	9.31 in.	2.50 in.
Maximum load	16,750 lbs.	92,290 lbs.	12,430 lbs.	73,680 lbs.
Crushing strength (lbs. per sq. in.)	1,404 lbs.	2,170 lbs.	1,105 lbs.	1,705 lbs.
Failure	Regular	Regular	Regular	Regular

Slagging Test

Specimens were heated to 1350°C, 2500°F, in a period of five hours. 12.6 grams of basic open hearth slag were then placed in the cavity previously prepared in the samples and held at the above temperature for two hours and allowed to cool in the furnace. Size of cavity, 1 $^5/_8$ in. diameter by $^9/_{16}$ in. depth.

Description of sample	Mottled	Brown
Slag used	Basic Open Hearth	...
Slag penetration, sq. in.	0.57	0.48

A test was made on each sample, using powdered silica brick and powdered magnesia brick. These materials showed no penetration under the above test.

The above slagging test is practically in compliance with the specification of the American Society of Testing Materials C 17–17 T, except the weight of slag and diameter of cavity. This was changed in order to permit the placing of three specimens in the furnace under the same conditions at the same time.

Chemical Analysis

Chemical analysis of portions of the three specimens subjected to fusion tests follows:

	White	Per cent mottled	Brown
Silica	44.90	46.62	47.50
Iron Oxide	0.71	0.71	4.60
Aluminum Oxide	52.39	50.91	46.36
Calcium Oxide	1.12	1.16	0.60
Magnesium Oxide	0.28	None	None
Sodium Oxide	0.04	0.24	0.26
Potassium Oxide	None	Trace	0.09
Titanium Oxide	0.10	0.28	0.60

Transverse Test

A transverse test was made on two samples of each, mottled and brown. The average of these two tests are:

Test	No. 1	No. 2
Description of sample	Mottled	Brown
Average dimensions	4.615 x 2.50 x 9.365	4.25 x 2.465 x 9.36
Distance between supports, C to C	8 in.	8 in.
Breadth as tested	4.615	4.425
Depth as tested	2.50	2.465
Maximum load sustained	1.140	1.390
Modulus of rupture	476	621

Specific Gravity

The determination of the specific gravity was made upon two specimens each of mottled and brown, the results of which are:

Test	Mottled No. 1	Brown No. 2
Weight used	60 grams	60 grams
Volume	21.1 cc.	21.1 cc.
Actual specific gravity	2.84	2.83

Conclusion

The above tests indicate a refractory with a very high fusion point and one that under temperature maintains its shape when subjected to pressure. It resists slagging action well, and the uniform penetration of the slag indicates a good mixture of the materials before molding. The absence of slagging with the magnesite brick and silica brick suggest that malinite refractories may be placed in contact with the other refractory materials without slagging action, and that the refractory possesses neutral properties.

Chester Shales

Shales belonging to the Sample, Elwren, Indian Springs, and other divisions of the Chester group of rocks in Indiana have been used for ceramic purposes. The quantity and the quality of the shales vary much in each stratigraphical horizon.

Physical Properties.—The Chester shales usually have a good degree of plasticity. The color is usually grey, greenish grey or maroon. The loss of weight in passing from the wet condition to the vitrified state is about 20%. The color of the more aluminous shales after reaching the vitrified stage is generally grey. The fusion point of the shales as taken from the outcrop of the better grades is from 2500°F to 3300°F. Mixtures of the shales and halloysite exhibit a much higher fusion point.

Chemical Composition.—The analyses of five samples of the Chester shales are given in the following table:

ANALYSES OF SAMPLES OF CHESTER SHALE

Constituents	No. 1, Per cent	No. 2, Per cent	No. 3, Per cent	No. 4, Per cent	No. 5, Per cent
Silica	61.24	64.57	58.40	58.68	59.67
Aluminium Oxide	18.38	18.67	20.70	21.39	19.75
Iron Oxide	4.76	6.22	6.58	6.22	7.32
Calcium Oxide	0.70	0.10	0.15	0.14	0.20
Magnesia	1.94	0.65	0.86	0.82	1.02
Alkalies	3.94	2.62	3.16	2.59	2.42
Loss on ignition	10.04	7.17	8.89	8.90	8.60
Sulphur Tri-oxide	.....	tr.	1.26	1.26	1.02
Total	101.00	100.00	100.00	100.00	100.00

By thoroughly weathering and washing the under clays and Chester shales they may be used in the manufacture of high grade refractories, but a better quality of refractory can be obtained by using a mixture of these clays and halloysite.

BLOOMINGTON, IND.

THE DEAD BURNING OF DOLOMITE.—III[1]

By James Thomas Robson and James R. Withrow

Survey of $Fe_2O_3.Al_2O_3.SiO_2$ Field as Dolomite Fluxes

After the preliminary work, it was decided to run series using $Fe_2O_3.Al_2O_3.SiO_2$ in all proportions that would be practically possible for dead burning dolomite. Four triaxial studies of twenty-two members were made similar to the previous work in 1A blending on the weight basis and using 100-mesh dolomite. Series C consisted of 95% of dolomite + 5% of flux, Series 2A contained 90% of dolomite + 10% of flux, the same as Series 1A. Series D consisted of 85% of dolomite + 15% of flux and Series E consisted of 60% of dolomite + 40% of flux. Series E was made in order to establish the fact that an excess of flux is undesirable. Series 2A was run in order to check up on 1A and also to compare this series with the three new series, it being burned and tested parallel with them.

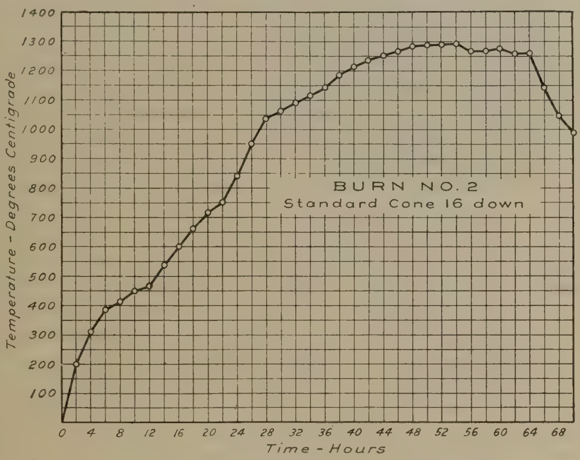

Fig. 18.

The percentage composition of the members of these series is given in Table V. These members were made as previously described for series 1A, using the same oxides as reported.

Six cubes of each member were set on magnesite brick and burned for 64 hours to cone 16 down. The temperature curve for this burn is shown in Fig. 18. The results are shown in Table VI.

As shown by the table, in general the high Fe_2O_3 field had what was termed "normal shrinkage;" the high Al_2O_3 field possessed the greatest shrinkage and the high SiO_2 field, the lowest shrinkage.

In Series C, all of the cubes appeared to be of good density and structure. Those containing Fe_2O_3 possessed a dull coke-like structure and appearance.

In general, the cubes in Series 2A appeared similar to those in Series C.

The cubes containing Fe_2O_3 in Series D appeared to be slightly more dense and vitrified than those in Series 2A. Member D17 had a slag-like appearance due to overfiring, D18 was also glassy due to overfiring. Members

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[1] Published by permission of the Director, U. S. Bureau of Mines. See "The Dead Burning of Dolomite.—I," *Jour. Amer. Ceram. Soc.*, 7 [1], 61 (1924).

TABLE V

	Series C 5% Flux, 95% Dolomite			Series 2A 10% Flux, 90% Dolomite			Series D 15% Flux, 85% Dolomite			Series E 40% Flux, 60% Dolomite		
Member	Fe_2O_3 per cent	Al_2O_3 per cent	SiO_2 per cent	Fe_2O_3 per cent	Al_2O_3 per cent	SiO_2 per cent	Fe_2O_3 per cent	Al_2O_3 per cent	SiO_2 per cent	Fe_2O_3 per cent	Al_2O_3 per cent	SiO_2 per cent
1	5	.	.	10	..	..	15	..	..	40	..	..
2	4	1	.	8	2	..	12	3	..	32	8	..
3	4	.	1	8	..	2	12	..	3	32	..	8
4	3	2	.	6	4	..	9	6	..	24	16	..
5	3	1	1	6	2	2	9	3	3	24	8	8
6	3	.	2	6	..	4	9	..	6	24	..	16
7	2	3	.	4	6	..	6	9	..	16	24	..
8	2	2	1	4	4	2	6	6	3	16	16	8
9	2	1	2	4	2	4	6	3	6	16	8	16
10	2	.	3	4	..	6	6	..	9	16	..	24
11	1.67	1.67	1.67	3.33	3.33	3.33	5	5	5	13.33	13.33	13.33
12	1	4	.	2	8	..	3	12	..	8	32	..
13	1	3	1	2	6	2	3	9	3	8	24	8
14	1	2	2	2	4	4	3	6	6	8	16	16
15	1	1	3	2	2	6	3	3	9	8	8	24
16	1	.	4	2	.	8	3	..	12	8	..	32
17	.	5	.	.	10	..	..	15	..	..	40	..
18	.	4	1	.	8	2	..	12	3	..	32	8
19	.	3	2	.	6	4	..	9	6	..	24	16
20	.	2	3	.	4	6	..	6	9	..	16	24
21	.	1	4	.	2	8	..	3	12	..	8	32
22	.	.	5	.	..	10	..	..	15	..	..	40

D20, D21 and D22 slaked down in the kiln due to an excessive amount of SiO_2 which tends to form dicalcium silicate.

The members of Series E all possessed a glassy surface due to overfiring. As shown in Table VI, most of the members of this series were either partially fused or fused down completely. All members were very much overburned showing that 40% of flux is too much for use of the dolomite as a refractory.

Member E19 appeared to be entirely different from any other members studied in that it gave a very white glassy partially fused cube containing long needle-like crystals throughout.

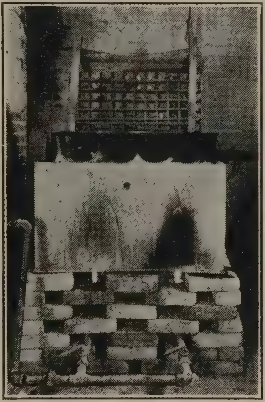

Fig. 19.—Warm water slaking test apparatus.

Tests

The room temperature and outside air slaking tests were run on this series similar to those of the preliminary tests. The hot water test, however, was made more reliable and uniform by using the tank and wire screen basket shown in Fig. 19. This tank contained 47 gallons of water which was maintained constantly at a temperature between 75–85°C. The level of the water was never allowed to fall below the surface of the basket so that the cubes were continuously immersed.

Fig. 20.—Autoclave.

The hot water test under pressure was run in the autoclave shown in Fig. 20. The cubes were placed in the autoclave, filled with water, and heated up to 21 pounds gage pressure, then removed and examined for signs of slaking or cracking. Those which withstood this test were then taken up to 50 pounds gage pressure, then to 97 pounds and finally to 103 pounds gage pressure which was the maximum pressure obtainable in this autoclave. After each pressure interval, the cubes which showed signs of breaking down or cracking were removed.

Air Slaking Test.—Both the outside and inside air slaking test proved to be of about the same rapidity in the case of Series C. Member C22 was the first to slake after 70 days' exposure at room and outside temperature. It swelled up to about three times its normal size, finally cracking and slaking down to a powder when pressed between the fingers.

Member C16 after exposure for 92 days in the laboratory, bloated to about $1^1/_2$ times its normal size and cracked badly. After 92 days' ex-

TABLE VI

RESULTS OF BURN AT CONE 16 DOWN

	Series C		Series 2A		Series D		Series E	
Member	Color	Remarks	Color	Remarks	Color	Remarks	Color	Remarks
1	Black	Normal shrinkage	Black	Normal shrinkage	Black	Excessive shrinkage	Reddish brown	Excessive shrinkage
2	Black	Normal shrinkage	Black	Normal shrinkage	Black	Excessive shrinkage	Brown	Excessive shrinkage
3	Black	Normal shrinkage	Black	Normal shrinkage	Black	Excessive shrinkage	Reddish brown	Excessive shrinkage
4	Black	Normal shrinkage	Black	Normal shrinkage	Black	Excessive shrinkage	Black	Excessive shrinkage
5	Black	Normal shrinkage	Black	Normal shrinkage	Black	Excessive shrinkage	Black	Excessive shrinkage
6	Black	Normal shrinkage	Black	Normal shrinkage	Black	Low shrinkage, very porous	Fused down completely	
7	Black	Normal shrinkage	Black	Normal shrinkage	Black	High shrinkage	Black	Partially fused
8	Black	Normal shrinkage	Black	Normal shrinkage	Black	High shrinkage	Dark brown	Partially fused
9	Black	Normal shrinkage	Black	Normal shrinkage	Black	Medium shrinkage	Fused down completely	
10	Black	Normal shrinkage	Black	Normal shrinkage	Black	Medium shrinkage	Fused down completely	
11	Black	Normal shrinkage	Black	Normal shrinkage	Black	Medium shrinkage	Fused down completely	

TABLE VI (*Continued*)

12	Black	Normal shrinkage	Black	Normal shrinkage	Black	High shrinkage	Black	Partially fused
13	Black	Normal shrinkage	Black	Normal shrinkage	Black	High shrinkage	Brown, glassy	Partially fused
14	Black	Normal shrinkage	Black	Normal shrinkage	Black	Medium shrinkage	Fused down completely	
15	Black	Low shrinkage	Black	Low shrinkage	Black	Medium shrinkage	Fused down completely	
16	Brownish black	Low shrinkage	Black	Low shrinkage	Slaked in kiln to brown powder		Brown	Partially fused
17	Light brown	Medium shrinkage	Light brown	High shrinkage	Brown	High shrinkage, very porous	Slaked in kiln to white powder	
18	Light brown	Medium shrinkage	Greenish brown	High shrinkage	Green, glassy	High shrinkage	Slaked in kiln to white powder	
19	Brownish green	Medium shrinkage	Pale green	Medium shrinkage	Pale green	Medium shrinkage	White frosty glass, many needle-like crystals present	
20	Brownish green	Low shrinkage	Green	Low shrinkage	Slaked in kiln		Slaked in kiln to white powder	
21	Green	Low shrinkage	Green	Low shrinkage	Slaked in kiln		Slaked in kiln to white powder	
22	Yellowish green	No shrinkage	Green	Low shrinkage	Slaked in kiln		Slaked in kiln to white powder	

posure outside, it swelled slightly and cracked badly although not as much as did the sample which was left at room temperature. Member C21 swelled and cracked badly after 102 days' exposure both inside and outside, although the sample kept inside swelled slightly more than the outside sample but did not crack as much.

Figure 21 shows these samples together with a cube of the original size before slaking started. The sample of C22 which underwent the outside air slaking test is not shown because it was broken when handled. The three cubes at the top are those which underwent the inside air slaking test, the two in the middle are those of the outside test and the bottom cube is one of original size.

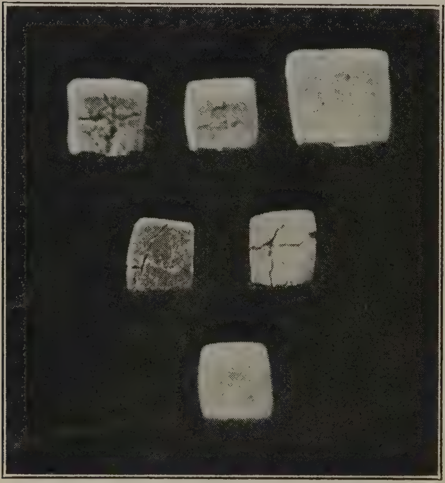
FIG. 21.—Air slaked cubes.

Member C6 slaked inside the room after 131 days but the outside sample has remained O. K. for 150 days.

As shown in Figs. 13 and 14,[1] several cubes in Series 1A had slaked after standing for 131 days, although Series 2A of the same composition had but one member, 2A1, which slaked both inside and outside after 131 days. After 150 days no other cubes in this series have slaked. This is probably due to the difference in atmospheric conditions. Series 1A was exposed during the summer months when the humidity is high, while Series 2A has been exposed during the winter months of low humidity.

In Series D, Members D15 and D4 have slaked after 131 days' exposure inside. No other member of this series has slaked after 150 days' exposure.

No member of Series E has slaked after 150 days' exposure.

Warm Water Slaking Test.—The results of this test are shown in Table VII and Figs. 22, 23, and 24.

Series C. –In the hot water slaking test, but two members, C18 and C19, appear to be reasonably stable. C18 withstood this test for 11 hours and C19 for 21 hours. Evidently 5% of flux does not give a very wide field of stability. See Fig. 22.

Series 2A.—As shown in Fig. 23, 2A13 and 2A20 were stable for 13 days. 2A15 stood up for 21 days and again as in the preliminary run,

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[1] See "The Dead Burning of Dolomite.—II," *Jour. Amer. Ceram. Soc.*, 7 [2], 144, 145(1924).

TABLE VII

WARM WATER SLAKING TEST

Number of Days before Slaking

Member	Series C	Series 2A	Series D	Series E
1	1	1	1	9
2	1	1	2	9
3	1	1	2	21
4	1	1	1	2
5	1	1	2	13
6	1	1	OK after 130 days	Slaked in kiln
7	1	1	1	Slaked in kiln
8	1	1	2	13
9	1	2	75	Slaked in kiln
10	1	2	13	Slaked in kiln
11	1	2	26	Slaked in kiln
12	1	4	9	Slaked in kiln
13	1	13	32	32
14	2	24	13	Slaked in kiln
15	1	21	50	Slaked in kiln
16	1	1	Slaked in kiln	Slaked in kiln
17	3	2	2	Slaked in kiln
18	11	2	21	Slaked in kiln
19	21	5	OK after 130 days	Slaked in kiln
20	1	13	Slaked in kiln	Slaked in kiln
21	1	2	Slaked in kiln	Slaked in kiln
22	1	2	Slaked in kiln	Slaked in kiln

Member 2A14 was the most stable member of the series, slaking after undergoing the test for 24 days.

This test is no doubt more severe than the boiling test conducted in the preliminary run where Member A14 withstood the test for 99 days.

In general, the field around Members 14, 15 and 20 appears to be the most stable as in the case in Series 1A.

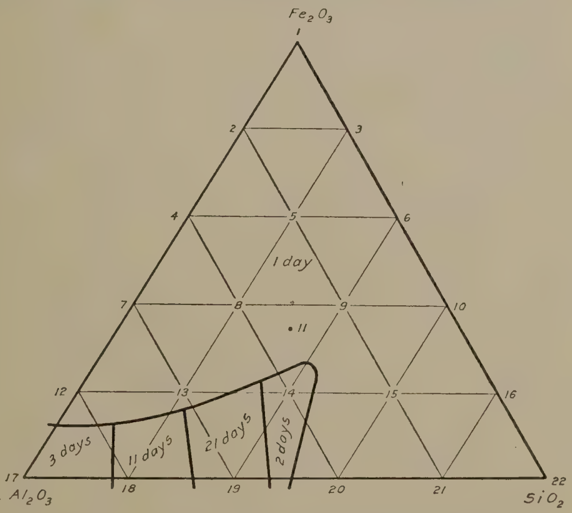

FIG. 22.—Warm water slaking test of Series C.

Series D.—Figure 24 shows that this series possesses a larger field of stability than series C and 2A. The field of low stability in this test lies on the $Fe_2O_3.Al_2O_3$ side especially in the high Fe_2O_3 region. The most stable field lies through the center of the diagram away from the apices, the most stable members being D6 and D19 which showed no signs of decomposition after 130 days.

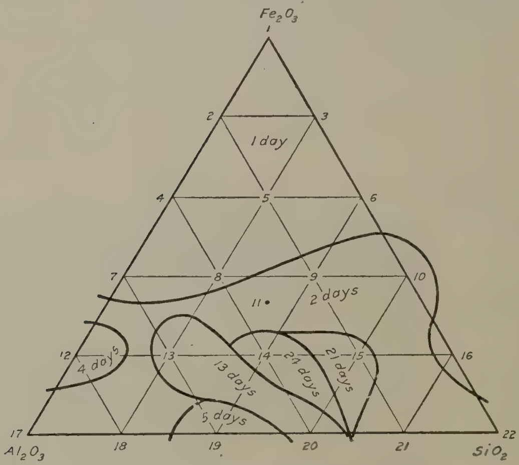

Fig. 23.—Warm water slaking test of Series 2A.

In this series there are seven stable members which underwent this test for more than 20 days. The extreme end members as in the other series, were very unstable.

Series E.—In this series, Member E1 stood up for 9 days, E3 was stable for 21 days, E5 and E8 did not slake until after 13 days and E13 stood up for 32 days. Member E19 withstood this test and did not slake after being subjected to this test for 130 days. As previously explained, E19 was partially fused at cone 16 so that it would probably be of no use as a refractory. Also, as previously shown, Member D19 failed to slake after 130 days test in warm water.

Because of the few members obtained in this burn, no definite conclusions on this test can be drawn. However, the tendency seems to be that the region high in Fe_2O_3 is again the most unstable.

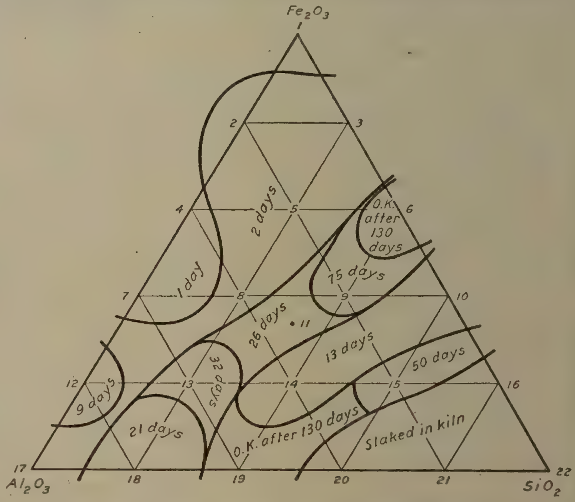

Fig. 24.—Warm water slaking test of Series D.

Hot Water Test under Pressure.—The results of this test are shown in Table VIII and Figs. 25, 26, 27.

Series C.—The results of this test on Series C are shown in Fig. 25. Here it is seen as in the other slaking tests, the most unstable area is in the high Fe_2O_3 field. The members in the low Fe_2O_3 region toward the Al_2O_3 field appear to be the most stable, Members C13, C14 and C17 did not slake when the gage pressure reached 103 pounds per square inch.

Series 2A.—The results for this series are shown in Fig. 26. The unstable field in this series is somewhat smaller than that in Series C but again lies in the high Fe_2O_3 area, the stable members lying in the low Fe_2O_3 field.

The Al_2O_3 content by itself, 10% in 2A17, seems to render the dolomite more unstable than did 5% Al_2O_3 in Member C17. Member 2A17 slaked down at 21 pounds pressure whereas C17 did not slake at the maximum pressure used, namely 103 pounds per square inch.

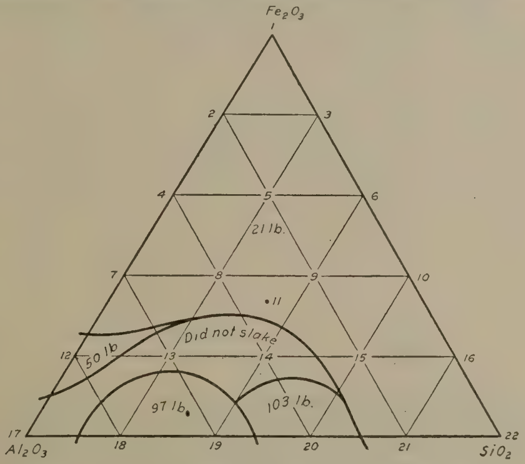

FIG. 25.—Hot water pressure test of Series C.

Although Member 2A17 is not included in the most stable area which did not slake in this series, the stable field is larger than that in Series C as will be seen by reference to Figs. 25 and 26.

TABLE VIII

HOT WATER SLAKING TEST UNDER PRESSURE

Number of pounds steam gage pressure applied before slaking

Member	Series C	Series 2A	Series D	Series E
1	21	21	21	21
2	21	21	Did not slake	Did not slake
3	21	21	Did not slake	. .
4	21	21	21	50
5	21	21	97	Did not slake
6	21	97	Did not slake	. .
7	21	21	21	. .
8	21	21	Did not slake	97
9	21	97	Did not slake	. .
10	21	Did not slake	Did not slake	. .
11	21	21	Did not slake	. .
12	50	Did not slake	97	. .
13	Did not slake	Did not slake	Did not slake	Did not slake
14	Did not slake	Did not slake	Did not slake	. .
15	21	Did not slake	Did not slake	. .
16	21	21	Slaked in kiln	. .
17	Did not slake	21	21	. .
18	97	97	Did not slake	. .
19	97	97	Did not slake	103
20	103	103	Slaked in kiln	. .
21	21	97	Slaked in kiln	. .
22	21	50	Slaked in kiln	. .

The stable field lies mostly below the 4% Fe_2O_3 of total flux line as is the case in Series C.

The extreme end members are very unstable under this test.

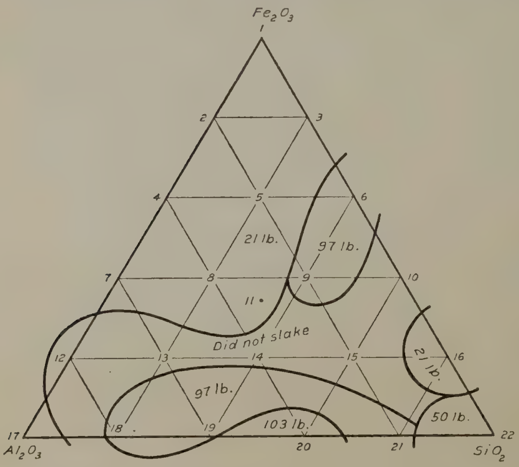

FIG. 26.—Hot water pressure test of Series 2A.

Series D.—Fig. 27 shows that 15% flux gives a much larger field of stability than 10% of flux as in Series A. The end members again appear to be very unstable.

Except in Member 2A2, it appears that at least a small amount of SiO_2 is required with the fluxes in order to make a stable composition.

As was the case in both Series C and Series 2A, Members D13 and D14 did not slake when the maximum pressure of 103 pounds per square inch was attained.

General Conclusions of Slaking Tests

In all series in these tests except in the test under pressure, two cubes of each member were tested and in every case both cubes slaked together, showing the results to be reliable. Wherever two cubes were used in the tests under pressure, they likewise slaked down together.

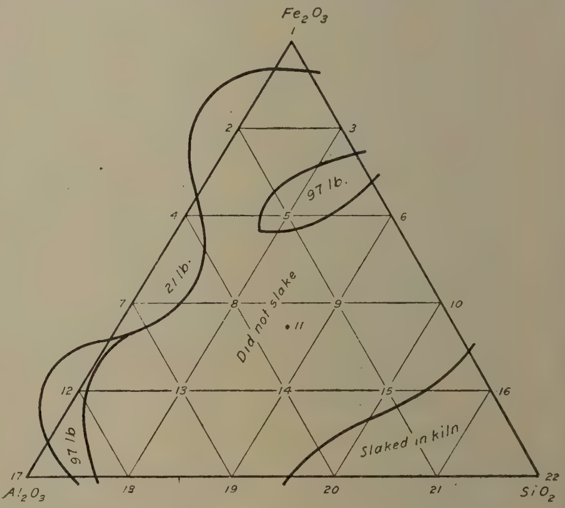

FIG. 27.—Hot water pressure test of Series D.

It will be noted that as the amount of flux increases, the area of the field of stability becomes larger so that, in general, increase in the amount of flux increases the stability of the dolomite.

Increase in amount of flux not only increases the area of the field of stability, but also the degree or length of time of stability, *e. g.*, the most stable member in Series C stood up in the warm water slaking test for 21 days, in Series 2A for 24 days and in Series D for more than 100 days.

Pure Fe_2O_3, pure Al_2O_3 or pure SiO_2 when used alone are of no value as fluxes for dead burning dolomite.

D6 containing only Fe_2O_3 and SiO_2 is very stable, likewise D19 containing only Al_2O_3 and SiO_2 is extremely stable. E19 is very stable, but it contains 40% of fluxes which, as shown later, have too great an effect on lowering the fusion temperature of dolomite to be used as a refractory.

Fusion Tests

Having determined the field of stability of these oxides as fluxes for dead burning dolomite, it was decided to make a study of the effect of these fluxes on the refractoriness of dolomite in order to determine what stable compounds appear plausible for using as refractories.

The ordinary cone fusion tests were run on all members of the three series, C, 2A and D. Since Series E appeared to be impracticable for commercial use because of its low fusing temperature as previously described, it was discarded from further work.

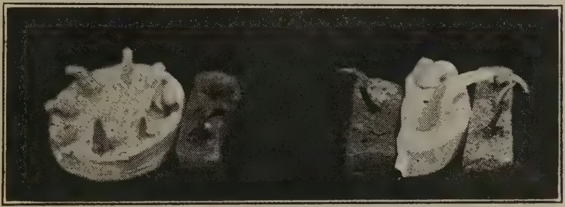
a *b*

FIG. 28.—Arrangement of cone plaques.

These dolomite cones fluxed violently at about cone 26 or lower when placed in the ordinary cone plaques made of sillimanite, bauxite or kaolin; so that it was found necessary to use two cone plaques for each burn. One plaque was made of calcined magnesite to hold the dolomite cones and for the standard cones an ordinary plaque of the following composition:

Florida kaolin	70%
Refined alumina	30%

This composition was tempered with water, formed into plaques, dried and calcined at cone 9.

The standard cones could not be placed in the magnesite plaque containing the dolomite cones, since it was found that they fluxed with magnesite at about cone 26 or lower.

The magnesite plaques were made of calcined magnesite. They were about $1\,^3/_4$ x $^1/_2$ x $^3/_8$ inches. Three holes about $^3/_{16}$-inch deep for holding cones were made in each plaque. These were calcined at about cone 8.

For preliminary tests in order to determine the approximate fusion temperature of the dolomite mixtures, ordinary round plaques 2 inches in diameter by $^3/_8$-inch deep with holes $^1/_8$-inch deep containing 8 standard cones ranging from cone 11 to cone 32 were made. These cones were varied with the different fields studied. These round plaques containing the standard cones together with a rectangular magnesite plaque containing three dolomite cones of different composition were placed together, side by side, on a magnesite block in a three-burner compressed air-gas pot furnace. These plaques together with their arrangement are shown in *a*, Figure 28. The furnace used is shown in Fig. 29.

The check determinations were run using 3 standard cones which were set in a sector broken from the ordinary round plaques. These sectors were about $^1/_2$-inch wide at the center. In many cases, two plaques of dolomite cones with the standard plaque placed between them were used. See *b*, Fig. 28.

The standard cones were held in place in the plaques with alumina powder. The dolomite mixture cones were held in place by powdered 100-mesh calcined magnesite. In order to prevent tipping of the cones, the magnesite powder was thoroughly tamped into the hole around the cone and then built up around it about $^1/_4$ inch high in order to fill the space formed due to greater contraction, during burning of the dolomite cones in comparison with the magnesite plaques containing them and also due to shrinkage of the magnesite powder itself.

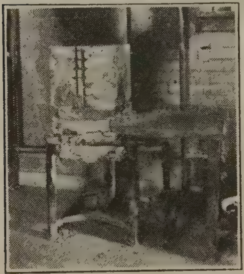

FIG. 29.—Fusion test furnace.

After these details had been adhered to, no trouble was experienced in running these tests.

In many instances, two cones of the same composition were placed in the same plaque and also during checking, cones of similar composition were placed in each of the two opposite plaques in order to assure that the temperature condition in the furnace was the same over the entire area covered by the three small plaques, which, as shown in *b*, Fig. 28, really occupied no wider area than the two plaques used in the preliminary tests.

Also, in several cases, a magnesite plaque containing dolomite cones was placed between two plaques of similar standard cones in order to frequently check on the uniformity of heat in the furnace. Cone 32 was the maximum temperature used in these tests, because of the excessive wear and tear on the furnace at temperatures higher than cone 32.

The cones used in these tests measured $1^1/_2$ inches in length, being made in the standard size cone mold and cut to this length. The standard cones below number 26 were also cut to this length.

Results of Fusion Tests

Series C.—Pure dolomite did not start to deform at standard cone 32 down. In Series C, all cones were standing straight up at cone 32 down, showing that 5% of these fluxes does not harm the deformation point of this dolomite.

Series 2A.—The deformation results in series 2A are shown on the triaxial diagram, Fig. 24. The shapes of these dolomite cones, when the standard cones numbered directly below were down, are shown on the diagram. Here it is seen that 10% of Fe_2O_3, alone as a flux, caused the dolomite to assume a position of about two o'clock at standard cone 32 down.

Member 17 consisting of 10% Al_2O_3 was the softest member of the series, it was down at standard cone 15 down. It started to deform with standard cone 12.

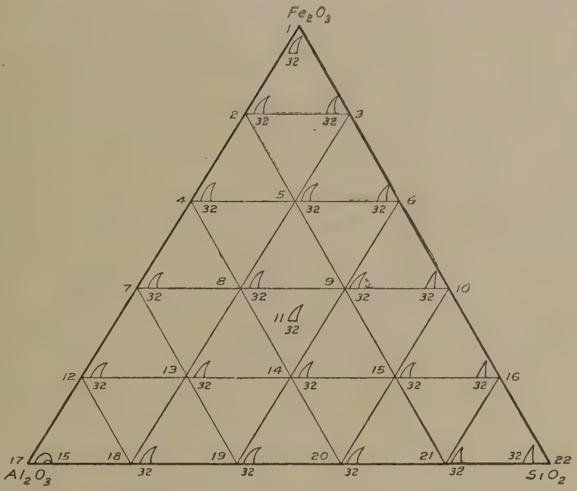

FIG. 30.—Fusion tests of Series 2A.

Member 22 containing 10% SiO_2 did not start to deform at standard cone 32 down.

There is no single eutectic mixture apparent between the three fluxes in this series, as the diagram shows. The high Al_2O_3 field appears to be the softest, the high Fe_2O_3 field next and the SiO_2 field is the hardest.

In every case where the cones stood at about two o'clock when standard cone 32 was down, the dolomite mixture cones started to bend between standard cones 20 and 23. After cone 26 was down, no further bending took place. This is probably explained by the fact that there was a sufficient amount of eutectic or low-melting mixture of fluxes present, to take enough dolomite into solution to cause the small tip at the top to lose shape and start bending, but the small amount of flux was not sufficiently active to cause the entire mass of dolomite to deform.

A study of the four component systems made up from the 3 component systems $CaO–MgO–SiO_2$; $MgO–Al_2O_3–SiO_2$; $CaO–Al_2O_3–SiO_2$ and $CaO–MgO–Al_2O_3$ given in the introduction, shows that it is to be expected that Al_2O_3 would have a more powerful solution action on the dolomite, because of the small field of stability of Al_2O_3.

The members along line 1–22 of zero Al_2O_3 in Fig. 30 show that Fe_2O_3

softens the mixture more than SiO_2 since 2A16 and 2A22 are perfectly straight up at cone 32 down while cone 10 is very nearly straight up and cones 2A1, 2A3, and 2A6 are about 2 o'clock at cone 32 down.

The line 2–21 in Fig. 30 shows that 2% Al_2O_3 in the presence of 8% of the other two oxides Fe_2O_3 and SiO_2 has about the same effect on the deformation temperature of dolomite as has 8% Al_2O_3 plus 2% of the oxides Fe_2O_3 and SiO_2 except in the case of 2A21 which has barely started to deform. Member 2A17 which contained 10% Al_2O_3 alone as previously mentioned, is much softer than the other members including 2A12 which contains 8% Al_2O_3 plus 2% Fe_2O_3 and Member 2A18 which contains 8% Al_2O_3 plus 2% SiO_2. This shows that 2% Fe_2O_3 or 2% SiO_2 has a decided hardening effect on Al_2O_3 as a flux for dolomite. Also since Member 17 in Series C was straight up at standard cone 32 down, the Al_2O_3 must be present in quantities over 5% before lowering this dolomite below a refractory of No. 1 grade.

Series D.—The deformation results in series D which consist of 15% flux plus 85% of dolomite are shown in the triaxial diagram, Fig. 31.

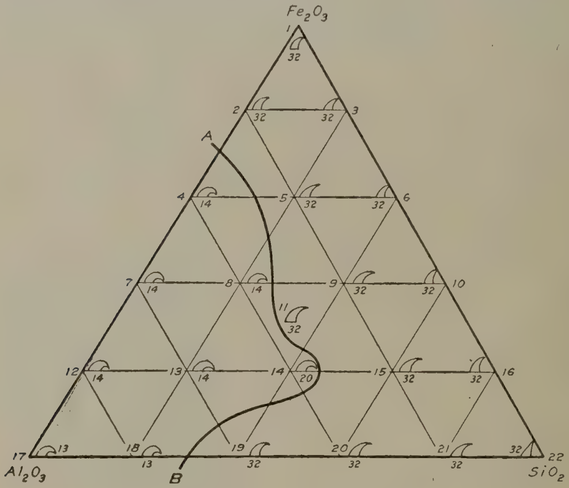

FIG. 31.—Fusion tests of Series D.

Member D1 containing 15% of Fe_2O_3 as a flux had a position of very nearly three o'clock at standard cone 32 down.

Member D22 containing 15% of SiO_2 alone as a flux again proved to be the most refractory, being very nearly straight up after standard cone 32 was down.

Likewise, as in Series 2A, Member D17 containing 15% Al_2O_3 was again the softest, being down when standard cone 13 was down.

This series compares with Series 2A in that the high SiO_2 is again the hardest, the high Fe_2O_3 field the next and the high Al_2O_3 field the softest.

By comparing the members of this series in the Al_2O_3 field to the left of line AB of the diagram, with similar members in Series 2A, it can be seen that 15% of flux where Al_2O_3 is present, has a much greater effect on the deformation temperature of dolomite than has 10% of these fluxes. All members in this region were down from standard cone 13 through standard cone 20 down.

Members D17 and D18 came down together, both started to bend when standard cone 10 was just down. Member D12 was slightly slower in deforming than Members D17 and D18.

The members to the right of line AB practically all started to bend between standard cones 20–23 down. After cone 26 was down, no visible deformation took place.

Figure 10[1] shows that 10% of SiO_2 lowers the fusion temperature of pure CaO.MgO from about 2380°C to about 2280°C and 15% SiO_2 lowers the fusion temperature to about 2200°C. Likewise, Fig. 9 shows that 10% Al_2O_3 lowers the fusion temperature of CaO.MgO from about 2380°C to only 2330°C and 15% Al_2O_3 lowers the fusion temperature to only about 2290°C. Comparing this action of SiO_2 and Al_2O_3, it is evident that 10% and 15% SiO_2 lowered the fusion point of pure CaO.MgO more than does 10% and 15% Al_2O_3, respectively. These curves cannot therefore be used comparatively as a criterion of the effect of these amounts of fluxes on the lowering of the deformation point of the dolomite studied herein since, as shown, Al_2O_3 has much greater effect in lowering the deformation of this dolomite than has SiO_2.

Since 15% of SiO_2, Member D22, had apparently no effect on the deformation of this dolomite, it may be that the fusion curve of the effect of SiO_2 on pure CaO.MgO may agree very closely with that showing the effect of SiO_2 on the deformation of this dolomite if this curve would have been determined by using sufficiently high temperatures.

Several members in each series of C, 2A and D were previously calcined to cone 5 and their deformation temperature determined. In all cases the deformation temperature found was the same as when the corresponding raw cones were tested for deformation.

In Series D where 15% of flux was used, there was a tendency for some of the members in the high SiO_2 field to form dicalcium silicate and hence decompose. Immediately after removing Members D16 and D21 from the pot furnace after heating to either cone 26 or cone 32, about $^1/_8$-inch of the top popped off the cone and the rest of it immediately slaked down into a fine powder. This happened in every case when these cones were removed from the furnace. Member D22 which contains 15% of SiO_2 alone as a flux did not slake as soon as D16 or D21 after heating to cone 26, but did slake after standing over night, evidently the formation of $2CaO.SiO_2$ was hastened by the presence of 3% Al_2O_3 or 3% Fe_2O_3.

(*To be continued*)

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[1] See "The Dead Burning of Dolomite.—I," *Jour. Amer. Ceram. Soc.*, 7 [1], 71 (1924).

¶ Members of the American Ceramic Society plan to take the Western Trip for the Summer Meeting, July 21 to August 16.

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ORIGINAL PAPERS

THE OXIDATION OF CERAMIC WARES DURING FIRING.—II. THE DECOMPOSITION OF VARIOUS COMPOUNDS OF IRON WITH SULPHUR UNDER SIMULATED KILN CONDITIONS[1]

BY FREDERICK G. JACKSON[2]

ABSTRACT

The progress of sulphur evolution is traced from a series of clay bars containing known amounts of various iron-sulphur compounds, both with and without the addition of carbon, when heated in imitation of a kiln schedule in atmospheres varying from pure oxygen to those commonly encountered in kiln practice, including neutral and reducing atmospheres. The varying degree of incompleteness of sulphur evolution is noted. The residual sulphur is found to be practically insoluble in water or aqua regia, but is rendered soluble by hydrofluoric acid. As a plausible explanation there is advanced the theory of the formation of "ferrous sulpho-silicate."

Introduction

In a previous paper[3] of this series the oxidation of carbon in a particular clay was discussed, and some rather striking facts were presented in connection with the evolution of sulphur by the clay. A series of conclusions of a tentative nature was added, but nothing very definite could be deduced from these results, since there are so many unknown factors entering into the problem, so the object of the work described in this present paper was to study this matter more fully.

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[1] Published by permission of the Director, U. S. Bureau of Mines.

[2] Associate Chemist, Ceramic Station, Columbus, Ohio.

[3] G. A. Bole and F. G. Jackson, "The Oxidation of Ceramic Wares during Firing.—I. Some Reactions of a Well-known Fire Clay," *Jour. Amer. Ceram. Soc.*, 7 [2], 163 (1924).

In burning a natural clay to make a ceramic ware the following factors may influence the nature and rate of evolution of sulphur from the ware:

1. Nature of the sulphur compound.
2. Grain size of the sulphur compound.
3. Amount of sulphur present.
4. Presence or absence of certain substances in the clay.
5. Structure of the clay.
6. Rate of heating the kiln.
7. Nature of the kiln atmosphere.
8. Rate of ventilation of the kiln.

In the experimental part of this investigation, the first five of these factors were controlled by using a very pure kaolin, to which was added known quantities of various impurities in imitation of natural clays. In general, the conditions employed were as close to kiln practice as possible. The rate of heating was on a progressive schedule in imitation of a kiln, and the atmospheres used at various times simulated the limiting and normal conditions in kiln practice.

Clay Used in Experiments

The clay used was a plastic kaolin, which gave the following analysis:

Constituent	Per cent	Constituent	Per cent
SiO_2	45.11	MgO	0.12
Al_2O_3	38.59	K_2O	0.00
Fe_2O_3	0.60	Na_2O	0.00
TiO_2	1.36	Sulphur	0.02
P_2O_5	0.03	Ignition loss	13.81
CaO	0.02		
			99.66

In order to study the reaction of each type of sulphur compound with iron, this clay was mixed in separate lots with ferrous sulphide, pyrite, ferric sulphate, ferrous sulphate, etc. The effect of grain size of the pyrite was also studied by using separate lots of 10- to 48-mesh and through 200-mesh. The effect of the presence of carbon on the sulphur in clay was also studied by making some test pieces containing ground coal or lamp black. For each case, 60 grams of clay were weighed and crushed. One and one-half grams of the iron-sulphur compound were then added, this being an amount of impurity frequently existing in natural clay, and, in some cases, 1.5 grams of carbon. These were ground carefully together and well mixed, then tempered with distilled water, thoroughly pugged, and rolled out into a bar. These bars were suitably numbered and air dried, then dried at 110°C for a week and kept in a desiccator.

Heating Schedule

In adopting a kiln schedule to a tube furnace of laboratory size, four factors had to be considered—namely, (1) the ratio of surface exposed to volume of clay; (2) the depth of penetration necessary; (3) the ratio of volume of gas to weight of clay; and (4) the rate of heating. The ratio of surface exposed to volume of clay is fifteen times as great in the tube furnace as in the face brick kiln, the schedule of which was simulated. The necessary penetration is only one-tenth as great. It therefore seemed proper, on passing to a laboratory scale, to divide the time of heating by ten, and the volume of gas per unit weight of clay per hour by two. This gave conditions that could be handled in the laboratory.

Since the clay was bone dry, it was possible in the laboratory to attain a temperature of 425°C in an hour. Therefore, by making a long day of it, it was possible to study the crucial part of the burn (425° to 775°C) in a single day's run.

A heating schedule was adopted from a commercial kiln and strictly adhered to throughout most of the experiments presented in this paper. This ran as follows:

Period, hours	Temp., °C	Period, hours	Temp., °C
1	425	6	615
2	445	7	665
3	480	8	720
4	510	9	775
5	560		

This schedule was modified in some cases so that 720° was attained in $7^1/_2$ hours and 775° in 8 hours. This did not affect the results, since reactions were practically complete by that time.

Temperature Measurement

To know the temperature under such conditions, a thermocouple must be in actual contact with the clay, rather than outside the tube, as in previous work. A noble-metal couple (platinum-platinum rhodium) will not register these temperatures so accurately, so a base-metal couple was inserted through the stopper at the intake end of the combustion tube, touching the end of the clay bar. A fused quartz combustion tube, drawn down to small bore at the outlet end, was used.

Absorption of Sulphur

Preliminary experiments showed that, with the large amount of water of combination in this clay, the previously used absorption apparatus would not do at all. Too much of the sulphur came off as sulphuric acid mist. Since sulphur was the object of the investigation, a method was sought of collecting this mist in a form that could easily be analyzed. The method adopted was to pass the gas from the combustion tube through damp asbestos. A short glass tube was connected to the outlet end of the combustion tube, and was bent at right angles downward. Onto the end of this a one-hole rubber stopper was slipped. This stopper sealed the top of a porcelain perforated (Gooch) crucible. In the bottom of the crucible was a thin asbestos mat. This condensed the sulphuric acid mist entirely, but was not attacked by it. The crucible was set in the customary way in a Gooch funnel, the end of which was bent at right angles. To this was attached a potash bulb, which was connected to gentle suction. This suction was necessary in order to get the gas through the asbestos mat without developing an excess pressure inside the combustion tube. Such a pressure would be unlike kiln conditions, and might change the course of reactions. A manometer was set in the intake line of the gas supply, and pressure was kept close to atmospheric by the regulation of valves. The apparatus is shown in Fig. 1.

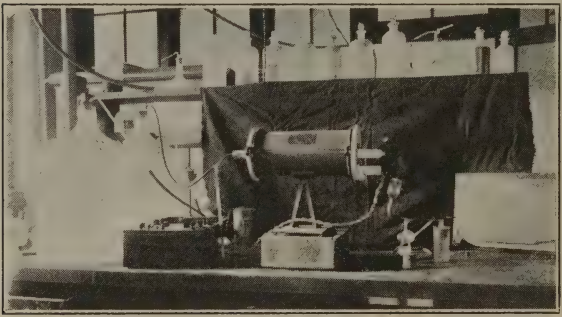

FIG. 1.—General view of apparatus.

At the end of each hour the incoming gas was stopped for a minute, the crucible and potash bulb were removed, and fresh ones were substituted and the gas flow continued. The used crucible was then rinsed by blowing three lots of distilled water through it. The washings were caught in a 100-cc. graduate flask. The Gooch funnel and the potash bulb were in turn rinsed into this flask, which was then filled to the mark with water, divided in two equal parts, and analyzed as before for SO_3 and SO_2.

Combustion Atmosphere

The atmosphere of a kiln may vary greatly under different conditions, and in order to study all possible variations, three different atmospheres were produced, a run being made with each on each class of impure or prepared clay. Pure oxygen was used, as being the extreme of oxidizing conditions. Then a mixture of 10% CO_2 and 90% air was used. This is similar to water-smoking conditions in a kiln when 200% excess air is passing, since there is about twice as much oxygen as CO_2. The third atmosphere was 10% CO_2, 50% air, and 40% nitrogen. This gives equal parts of CO_2 and oxygen, and corresponds to the best conditions in the middle of a burn, when there is 100% excess air in the flue gas. Oxidized iron-sulphur compounds were also studied in an atmosphere of pure nitrogen, and in an atmosphere of 90% nitrogen, and 10% hydrogen. It will be shown that the nature of the atmosphere has a marked effect on the burning. These mixed atmospheres were prepared in graduated 5-gallon bottles by adding the desired quantity of gas from a tank to a bottle full of water, while the bottle was being drained by syphon. Air was similarly drawn from the room. The mixed gas was forced out by a slow stream of water that was forced in. Since the gas did not bubble through the water, and the water was not agitated and was in contact with gas for only a few hours, the amount of CO_2 dissolved by the water was negligible.

Procedure

A typical day's run of the process was as follows: The cooled bar from the previous day was removed from the combustion tube and weighed. The new bar, dried at 110°C, was then weighed and put into the tube, the current turned on, and the rheostat set so that the temperature would reach 425° in an hour. A fresh absorption train was attached, and the gas flow started. The gas flow and the suction were so adjusted that the pressure remained atmospheric in the tube, and the speed of gas passing was correct. The filtration, ignition, and weighing of the 18 barium sulphate precipitates of the previous day were then begun and completed during spare moments of the day. At the time that 425° was reached the rheostat was cut back. Adjustment was made in accord with frequent temperature readings thereafter, so that the heating schedule was maintained. At the end of each hour the absorption train was changed. The spent one was then rinsed out, refilled, and placed in readiness.

The flasks containing rinsings were numbered and set aside. When sufficient had accumulated, they were each filled to the mark with distilled water and each emptied into a beaker so as to mix thoroughly. From each beaker 50 cc. were measured out in a graduate and put into a second beaker, all beakers being properly marked. The graduate and graduated flask were then rinsed into the beakers. Half of the beakers were then each neutralized with an excess of HCl and boiled for five minutes. In some cases the smell of SO_2 evolved was quite noticeable. When this was gone, barium chloride solution was slowly added to the boiling liquids until precipitation was complete. The beakers were then removed and allowed to stand over night, so that the $BaSO_4$ was in proper condition to filter. The remaining beakers were then neutralized with concentrated nitric acid in excess, and bromine water was added. These two powerful oxidizing agents converted all SO_2 to SO_3. In a few cases, as will be described later, H_2S was formed to some extent. The HNO_3 first precipitated this as sulphur. Bromine water on standing would dissolve and oxidize this to H_2SO_4. This sulphur precipitate would also be formed from H_2S in the beaker neutralized with HCl. It was allowed to remain, since it burnt off completely on igniting the precipitate.

After the bromine color had persisted for five minutes, $Ba(NO_3)_2$ solution was added. The liquid was then boiled until free of bromine color, and until the addition of more $Ba(NO_3)_2$ solution did not increase the precipitate. It was then also set aside over night, after dilution to a volume of about 200 cubic centimeters.

On account of difficulty in starting the precipitation of $BaSO_4$ in the presence of HNO_3, this procedure was later modified. Bromine water in excess was added to the alkaline solution, HCl then added, and precipitation was effected, after boiling, with $BaCl_2$.

In the meantime, the temperature was being watched and maintained, pressure regulated, absorption trains washed out and prepared and changed at the proper times, and new gas mixtures prepared as required.

Determination of Evolved Hydrogen Sulphide

When conditions were temporarily reducing in some of the early experiments, the evolution of some H_2S was noticed. No effort was made at first to determine this separately from SO_2, but the two were oxidized together and determined as $BaSO_4$.

The quantitative determination of H_2S appeared of importance in some cases. Accordingly, the absorption apparatus was modified on occasion so that the gas from the combustion tube first bubbled through a solution of cadmium chloride, then passed on through the customary Gooch crucible with asbestos mat and potash bulb. At the end of each hour this train was replaced with a fresh one. The cadmium chloride solution was then examined for sulphide, and if any of this yellow precipitate was seen, it was filtered out and washed. The filter paper and precipitate were then put into a beaker of distilled water, pulped with a glass rod, a little starch paste added, then an excess of HCl added, and the liberated H_2S at once titrated with a standardized iodine solution. This iodine was stored in a bottle painted black, from which it was forced by air pressure through all glass connections to a burette. But in spite of these precautions to keep iodine away from light and rubber, the solution deteriorated slowly, and required daily comparison with a standard sodium thiosulphate solution. With this comparison as a basis, the sulphur content of each CdS precipitate was calculated; SO_3 and SO_2 were then determined as usual in the filtrate of the CdS precipitate, to which the caustic soda and washings of the Gooch crucible had been added.

Possible Sources of Error

There are many possible sources of error in the apparatus, which were guarded against as follows:

1. Sulphur compounds might be in the gases forced into the combustion tube: The oxygen and nitrogen were tested and found to be sulphur free. The CO_2 was passed through limestone chips, and the room was aired before drawing in air in case the atmosphere seemed the least tainted.

2. Sulphur might be generated from the rubber stopper in the intake end of the combustion tube; however, it survived 25 runs without evidence of any charring. Also some of the runs made showed no sulphur evolved at the highest temperatures, when such action would be most likely to occur.

3. Sulphur-bearing gases may be lost in changing absorption trains. The inflow of gas was always first stopped. Then the crucible was loosened from the rubber stopper, and held close to it for a few moments with suction running. This drew in any gas that might still come from the tube and all that was inside the crucible.

4. Sulphuric acid mist may pass through the asbestos pad and fail to be absorbed, due to a hole in the mat: This actually happened on three occasions. It could be detected at once because white smoke gathered in the potash bulb as soon as the gas flow started. In these cases the gas flow was stopped again at once, the crucible detached, and a little more asbestos pulp poured into it. The suction formed this into a perfect mat at once. The small amount of mist that had passed the mat was naturally diluted with mist-free gas before reaching the soda solution, and was practically all absorbed so that the loss was negligible.

5. Sulphur dioxide may not be completely absorbed by the soda solution; tests, with a second bulb added, proved that absorption was complete. The gas in all cases bubbled through four successive reservoirs of solution. There was a large excess of soda present, so that although in some cases nearly 0.5 gram of SO_2 was absorbed in a single hour, as well as the CO_2 that was passing, this excess was only slightly impaired.

Presentation of Results

By following the method described above as applied to each variety of impure or prepared clay with each atmosphere, considerable data were obtained. Simplification was necessary before presentation. Accordingly, the weight of SO_3 or SO_2 found to have been evolved in each hour was recalculated to the corresponding weight of sulphur. Then was calculated what percentage this was of the total sulphur added to the clay. The percentage per hour of the total sulphur evolved both as SO_3 and as SO_2 is shown in tabular form in each case. This is followed by curves, which show the cumulative evolution of sulphur. In each case the lower curve shows the SO_3, and the area subtended by the curve shows the amount so far evolved. The upper curve shows SO_2 plus SO_3. The area between curves shows the amount of SO_2 evolved. Where H_2S was measured, this is similarly added above in a third curve. In all cases that appeared at all abnormal, the results were checked by repeating the experiment.

Interpretation of Results

Ferrous Sulphide in Clay.—Although FeS does not occur naturally in raw clay, it was studied in this series of experiments because it is in al probability formed as an intermediate product in the oxidation of pyrite

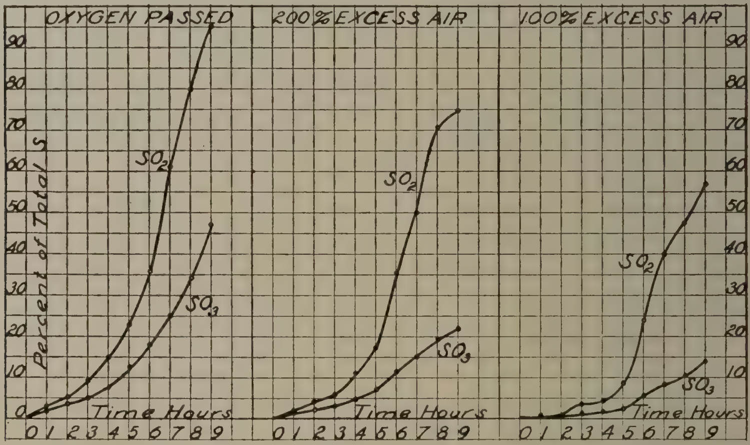

FIG. 2.—Ferrous sulphide.

Its behavior is the simplest, and will, therefore, be considered first. When treated with pure oxygen, it begins to oxidize at low temperature by the reaction

$$4FeS + 9O_2 = 2Fe_2O_3\text{[1]} + 4SO_3$$

Since this reaction does not generate appreciable heat, it proceeds slowly. As the action proceeds at increasing temperatures there is an increasing tendency for the SO_3 already formed to give up one of its atoms of oxygen to burn more FeS in this manner:

$$2FeS + 7SO_3\text{[1]} = Fe_2O_3\text{[1]} + 9SO_2\text{[1]}$$

There is also the possibility of direct formation of SO_2 as follows:

$$4FeS + 7O_2 = 2Fe_2O_3\text{[1]} + 4SO_2$$

[1] There may well be an intermediate stage in which at first a lower oxide of iron such as Fe_3O_4 is formed. This will later oxidize to Fe_2O_3. This step is omitted for simplicity in these reactions.

The resultant of these forces, in the case of oxygen, is an evolution of almost equal parts of SO_3 and SO_2, very close to 47% of the total sulphur being evolved in each way. There seems to be little, if any, other action. Appearances are all to the effect that, if heating had been continued at the same rate for another hour, all of the sulphur would have been evolved.

When we cut down the oxygen content of the gas passing to about 18%, the oxidation of sulphur is retarded. There is also, naturally, the tendency for the reactions using less oxygen to predominate. Thus we have 21% of the sulphur going off as SO_3 and 53% as SO_2 in the course of this run. The general trend of the burning remains unchanged. There is only a slowing up of the actions.

On still further cutting down the oxygen content, this slowing up is still more marked. Only 13% of the sulphur comes off as SO_3 and 43% as SO_2. The general tendency of the curves (Fig. 2) is not, however, altered in kind, but only in degree. It must be remembered that, even in this case, there is a little more than enough oxygen passing during each hour to convert all of the sulphur added to the clay into SO_3.

TABLE I

RESULTS OF TREATMENT OF CLAY WITH FERROUS SULPHIDE

Time, hours	Temp., °C	Oxygen		200 per cent excess air		100 per cent excess air	
		SO_3	SO_2	SO_3	SO_2	SO_3	SO_2
1	425	2.19	0.29	1.32	0	0	0
2	445	0.99	1.18	0.68	1.21	0	0
3	480	1.31	2.48	0.87	1.32	0.49	2.20
4	510	2.79	2.07	1.50	3.69	0.30	0.27
5	560	4.92	4.30	2.39	3.98	0.62	3.89
6	615	5.65	7.45	4.24	13.52	2.38	11.81
7	665	6.65	19.23	3.88	10.43	2.52	13.58
8	720	9.20	9.35	4.04	16.85	2.13	5.07
9	775	13.10	2.35	2.22	3.75	3.67	6.31
	TOTALS	46.80	48.70	21.41	54.75	12.11	43.13
Total per cent sulphur evolved		95.50		76.16		55.24	

Fine Pyrite in Clay

When fine FeS_2 is burned in clay in an atmosphere of oxygen, what amounts almost to an explosion takes place at just about 425°. The reaction $FeS_2 + O_2 = FeS + SO_2$ generates a considerable amount of heat. Once it has started, it raises the temperature of the surrounding clay, and runs with rapidity to completion. There are a number of additional reactions that may take place, due to this sudden heating, such as—

$4FeS + 9O_2 = 2Fe_2O_3 + 4SO_3$
$4FeS + 7O_2 = 2Fe_2O_3 + 4SO_2$
$4FeS + 6O_2 = 4FeSO_4$, or some similar compound.

The very fact that more than half of the total sulphur present is evolved during the first two hours proves that some second reaction takes place by which some of the second atoms of sulphur are liberated. Beyond this point the gas evolution proceeds as if there were a mixture of FeS and $Fe_2(SO_4)_3$ present. This may well be the case. If molecules of FeS have started to oxidize without losing their sulphur, they would probably behave similarly to $Fe_2(SO_4)_3$ molecules on further heating.

When air containing 10% CO_2 was passed, the procedure was changed but little. The first explosion was slightly damped, only 58% of the sulphur coming off in the first two hours, as compared with 62% in the previous case. A little less of this was SO_3 than in the first case. This would be expected with less oxygen present. In this case either the heating was a trifle faster or the change of absorption trains was not made at exactly the same moment, so that the bulk of SO_2 was caught in the first hour rather than in the second. This difference should be set down to experimental inaccuracy. It is evident from laboratory observation that almost all of this gas is generated and absorbed between 50 and 70 minutes after the heating is started. The curve (Fig. 3) of gas evolution from then on closely resembles that of ferrous sulphide under similar conditions. More SO_2 and less SO_3 is generated than in the last case when oxygen was more abundant. Also, actually more sulphur is evolved. The difference of 4% after 2 hours becomes 1.5% after 9 hours. This would be expected if less of the ferrous sulphide were oxidized by the "explosion" to some iron-sulphur-oxygen compound. This was probably the case, since the explosion was less violent.

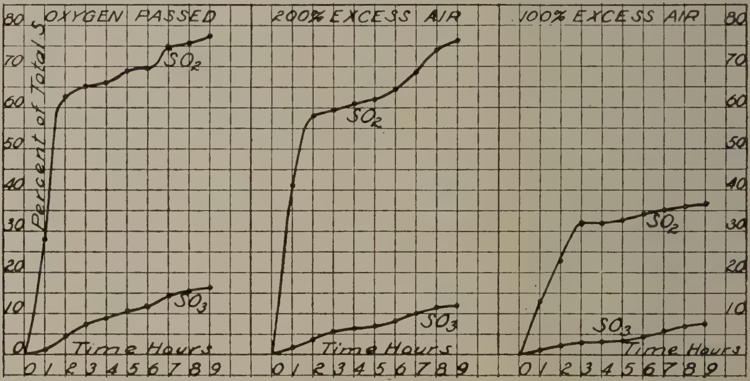

FIG. 3.—Fine pyrite.

When the amount of oxygen in the gas was still further reduced, the first explosion was greatly retarded. It took place during parts of the first three hours, and not even all of the first atoms of sulphur were evolved then. During the fourth hour the evolution of sulphur was very slight. It was also noticed on neutralizing the caustic soda which was used to absorb the SO_2 that no CO_2 had come through the combustion tube. The sulphur in the clay must have been very eager for oxygen to have decomposed CO_2 to CO. It is possible that a hyposulphite of iron was forming, with two atoms of sulphur to each atom of iron, similar to FeS_2O_3, although no such compound has ever been isolated. A more reasonable explanation, however, lies in the fact that the original clay, the purest obtainable, contained 0.60% of iron. This iron was probably originally oxide and absorbed some of the SO_2 which had been liberated from the FeS_2. Due to the comparatively limited oxygen supply, it is probable that the iron-sulphur-oxygen compound formed is not ferric sulphate to any great extent, but some ferrous compound. However, the sulphur evolution during the rest of the run was only from 31 to 36%, and almost all of this was SO_3. There seems to be some reaction going on here which is not yet explained, and this will be studied later.

TABLE II

RESULTS OF TREATMENT OF CLAY WITH FINE PYRITE

Time, hours	Temp., °C	Oxygen		200 per cent excess air		100 per cent excess air	
		SO_3	SO_2	SO_3	SO_2	SO_3	SO_2
1	425	0.86	26.90	1.21	39.80	0.62	11.78
2	445	3.72	30.80	2.12	14.30	1.37	8.70
3	480	2.57	0	1.87	0.20	0.53	8.42
4	510	0.91	0.15	0.74	0.10	0.12	0.31
5	560	2.50	0.30	0.84	0.10	0.37	0.22
6	615	0.65	0.25	1.14	0.50	0.95	0
7	665	3.25	2.10	1.51	2.30	1.31	0
8	720	0.79	0	1.64	4.20	1.08	0
9	775	1.29	0.40	0.81	1.50	0.60	0
TOTALS		16.54	60.90	11.88	63.00	7.01	29.43
Total per cent sulphur evolved		77.44		74.88		36.44	

Fine Pyrite with Lamp black

When pyrite and lamp black are mixed in clay and burned in oxygen we have all of the ingredients of old-fashioned gunpowder—namely, sulphur, charcoal and oxygen. It is little wonder, therefore, that when this reaches its ignition temperature it burns with a rush. Over 64% of the sulphur came off in the first hour, nearly all as SO_2. The last portions of this burning were completed in the next two hours, making a total of 84% of the sulphur evolved. After that only traces of sulphur came off, practically all as SO_3.

With the normal kiln atmosphere, a more satisfactory combustion takes place. The conditions of pyrite and lamp black burned in 90% air and

10% CO_2 are very similar to kiln practice on a normal fire clay. Here the explosion takes place more slowly. There is not enough oxygen to burn all of the lamp black rapidly.

It was earlier stated that there was a little more than enough oxygen passing when 100% excess air was used to burn all of the sulphur in 1.5 grams of FeS in one hour. While this is true, it must be realized that to burn 1.5 grams of carbon requires much more oxygen. It requires all of the oxygen passed for three hours to convert this carbon to CO.

During the fourth hour a little of the sulphur came off as H_2S. This could happen by any of several reactions such as—

$$SO_2 + 3CO + H_2O = H_2S + 3CO_2$$
$$FeS + H_2O = H_2S + FeO$$

Conditions appeared to be so well adjusted in this burn that the greatest yield of sulphur gas was obtained of any of the pyrite burns.

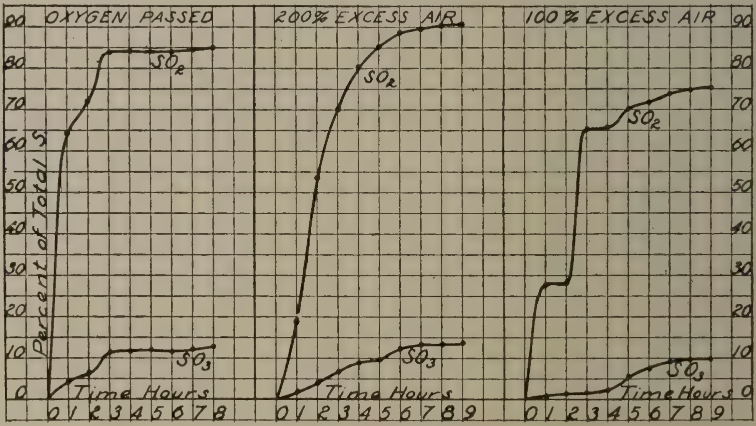

FIG. 4.—Fine pyrite and lamp black.

With the minimum oxygen supply, an interesting analysis of the explosion is shown. Reverting to the analogy of gunpowder, it is well known that sulphur was not desired in gunpowder. It formed fumes which corroded the gun barrel, but it ignited at a lower temperature than carbon, and so was put in to make the explosion start more readily. In this experiment we see 27% of the sulphur burnt off in the first hour, and none in the second hour; also in the second hour no CO_2 was evolved. Therefore, the sulphur must have "caught fire" first, and heated the lamp black up to its ignition point. The CO then formed smothered the burning of the sulphur completely for the space of the second hour, then sulphur again burned in the third hour, until over 65% was gasified, and, therefore, the most readily combustible part of it was all gone. Then followed a period of oxidation through the fourth hour, with little evolution of sulphur and complete reduction of CO_2. This was followed by the now familiar phenomenon of only a few per cent of the remaining sulphur being evolved through the rest of the run, and mostly as SO_3. (See Fig. 4.)

TABLE III

RESULTS OF TREATMENT OF CLAY WITH FINE PYRITE AND LAMP BLACK

Time, hours	Temp., °C	Oxygen		200 per cent excess air		100 per cent excess air	
		SO_3	SO_2	SO_3	SO_2	SO_3	SO_2
1	425	4.28	59.70	1.65	16.73	0.47	26.70
2	445	1.71	6.10	1.97	32.52	0.11	0[2]
3	480	5.22	6.30	3.17	13.44	0.75	36.90
4	510	0.10	0	1.56	8.70[1]	0.29	0.60[2]
5	560	0.18	0	0.63	3.97	3.61	1.00
6	615	0.12	0	2.97	0.85	1.48	0
7	665	0.37	0	0.55	0.41	1.74	0
8	720	0.16	0.15	0.29	0.45	0.39	0.70
9	775	0.27	0	0.48	0	0.33	0.30
TOTALS		12.41	72.25	13.27	77.07	9.17	66.20
Total per cent sulphur evolved		84.66		90.34		75.37	

[1] H_2S noted.

[2] No CO_2 caught.

Coarse Pyrite

When coarse FeS_2 was burned in oxygen it did so more slowly than the fine pyrite. The grains were larger and fewer, and therefore farther apart; and so the original spark of combustion may not have been transmitted as rapidly. For that reason the furnace would be hotter, when the burning was taking place and the gas evolution was, therefore, greater.

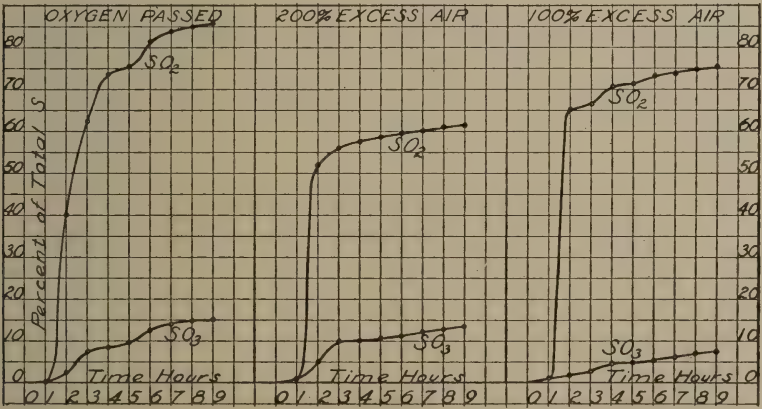

FIG. 5.—Coarse pyrite.

When heated with the normal kiln atmosphere of 200% excess air, the burning of sulphur had just begun at the end of the first hour. A little over 50% of the sulphur came off in the first two hours, almost all as SO_2. During the third hour the evolution of SO_2 came to an end, and the SO_3 continued to be given off slowly until the end of the run.

When the minimum oxygen supply was furnished to coarse FeS_2, a most surprising evolution of 65% of the sulphur as SO_2 took place during the second hour. Followed the customary periods of oxidation, when during the third and fifth hours almost no sulphur and no CO_2 came off, between which, during the fourth hour, 1.6% of the sulphur as SO_3 and twice as much as SO_2 was evolved. After this, only 3% of the sulphur came off during the rest of the burn. Almost all of this was as SO_3, as usual. (See Fig. 5.)

TABLE IV

RESULTS OF TREATMENT OF CLAY WITH COARSE PYRITE

Time, hours	Temp., °C	Oxygen		200 per cent excess air		100 per cent excess air	
		SO_3	SO_2	SO_3	SO_2	SO_3	SO_2
1	425	0.32	0	0.69	0.75	0.44	0.17[1]
2	445	1.81	38.50	4.17	47.00	1.30	63.08
3	480	5.16	16.80	4.55	4.10	0.21	0[1]
4	510	1.48	9.50	1.03	0.10	1.63	3.35
5	560	0.96	1.20	0.49	0.20	0.11	0[1]
6	615	2.57	3.40	0.57	0.10	1.24	0.65
7	665	1.13	1.10	0.86	0.40	0.45	0
8	720	0.67	0.25	0.35	0	0.80	0
9	775	0.63	0.50	0.62	0	0.73	0.30
TOTALS		14.73	71.25	13.33	52.65	6.91	67.55
Total per cent sulphur evolved		85.98		65.98		74.46	

[1] No CO_2 caught.

Coarse Pyrite with Lamp Black

When this mixture was heated in oxygen, the first spark of combustion which did not occur until after the first hour, was rapidly propagated throughout the clay by the lamp black. Therefore, as much sulphur came off during the second hour alone as during the second and third in the experiment where carbon was absent. By this time the lamp black was all burned out, and the behavior of the remainder of the two burns was very similar. The final yields in the two cases were almost identical.

With the normal kiln atmosphere of 200% excess air the yield was 6% better than when lamp black was absent under similar circumstances. The SO_3 was less, due to the reducing conditions. After the fifth hour no SO_2 and very little SO_3 was given off.

With the atmosphere lowest in oxygen content, the main sulphur evolution was spread out through five hours. However, the yield was higher than in the former case, and SO_2 continued to be formed throughout the burning time. During the second, third, and fourth hours, H_2S was formed to some extent. Apparently, conditions were such that only disulphide and sulphide can exist as solids. These compounds then decompose to H_2S and SO_2. (See Fig. 6.)

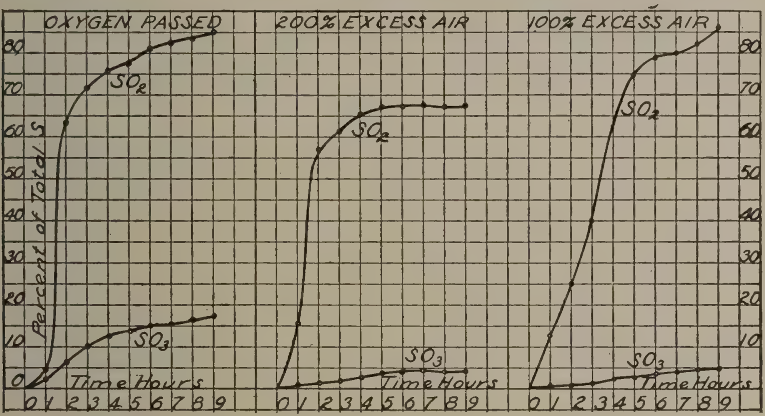

FIG. 6.—Coarse pyrite and lamp black.

TABLE V

RESULTS OF TREATMENT OF CLAY WITH COARSE PYRITE AND LAMP BLACK

Time, hours	Temp., °C	Oxygen		200 per cent excess air		100 per cent excess air	
		SO_3	SO_2	SO_3	SO_2	SO_3	SO_2
1	425	2.40	2.25	0.76	16.50	0.19	11.19
2	445	3.95	54.90	0.43	39.80	0.39	11.76[1]
3	480	3.91	4.30	0.23	3.20	0.97	15.45[1]
4	510	1.98	2.65	1.48	2.90	0.55	20.60
5	560	0.85	0.40	0.49	1.10	0.71	10.80
6	615	1.57	2.30	0.23	0	0.48	3.90
7	665	0.69	0.35	0.28	0	0.61	1.00
8	720	1.16	0.40	0.09	0	0.33	1.70
9	775	0.58	0	0	0	0.64	3.40
TOTALS		17.09	67.55	3.99	63.50	4.87	79.50
Total per cent sulphur evolved		84.64		67.49		84.37	

[1] H_2S noted.

(The second part of this paper will appear in the May Journal)

THE SYSTEM: $Al_2O_3.SiO_2$

By N. L. Bowen and J. W. Greig[1]

ABSTRACT

This paper deals with a study of the equilibrium relations of mixtures of pure alumina and silica at high temperatures. The results are expressed concisely in the form of an equilibrium diagram and their bearing on ceramic problems is discussed.

The principal feature of the diagram is the absence of the compound $Al_2O_3.SiO_2$, the only compound being $3Al_2O_3.2SiO_2$. Crystals of this latter compound occur in all alumina-silica refractories. The optical properties of these crystals have been determined and are compared with those of sillimanite, $Al_2O_3.SiO_2$, which has hitherto been regarded as the crystalline compound occurring in refractories and clay bodies in general.

The behavior of natural sillimanite on heating is discussed.

Introduction

Clay, the great raw material of the ceramic industry, may be regarded as consisting essentially of hydrous silicates of alumina. Many clays are, to be sure, very impure and their properties depend upon the impurities to a considerable extent, but the better grades contain little else than silica, alumina, and water, so that a knowledge of the behavior of alumina-silica mixtures at high temperatures is fundamental to an understanding of the behavior of such clays at these temperatures. Especially is this true at the present time when so much experimentation is going forward in the production of highly refractory wares involving the use of special clays and of mixtures imitating in composition the natural mineral sillimanite, $Al_2O_3.SiO_2$, which composition is believed to have special virtues.

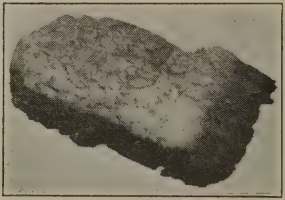

Fig. 1.—Fragment of tank block showing thick crust of corundum (dark) formed by the action of glass on the clay body.

A knowledge of the behavior of alumina-silica mixtures at elevated temperatures is of no less importance to the geologist, for these same clay materials are frequently heated under natural conditions and the geologist must strive to interpret the changes which they have undergone. Indeed it was largely from geologic considerations that the impetus came for a reinvestigation of the alumina-silica system. Shales and related rocks when heated as a result of immersion in igneous magmas often have free alumina, as corundum, developed in them by reaction with the magma. This may be true even when the total compositions indicate an ample supply of silica to form sillimanite,[2] $Al_2O_3.SiO_2$. Development of corundum under quite similar conditions may occur where artificial silicate melts (glasses) react with refractory clay bodies at their mutual contact surfaces. An excellent example of this is shown in the photograph, Fig. 1. Now the most probable interpretation of this setting-free of corundum is that sillimanite itself melts incongruently, breaking up into corundum and liquid. The system $Al_2O_3.SiO_2$ had formerly been investigated at this Laboratory, the problem being among the very earliest studied here. The results then obtained were believed to show a maximum or congruent melting point (1816°) at the composition of sillimanite with a eutectic between sillimanite and corundum (1810°). (See Fig. 2.)[1] The difference between these temperatures is less than the limit of error of measurement at such temperatures and on such materials, so that the existence of a eutectic cannot be regarded as definitely proved. The possibility of incongruent melting is therefore not altogether precluded. Further investigation of this point was thus indicated and was accordingly undertaken.

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[1] Presented at the Atlantic City Meeting, Feb., 1924. (Refractories Division.)

[2] H. H. Thomas, "The Best Described Examples Are Those from the Island of Mull," *Quar. Jour. Geol. Soc.*, **78**, 229 (1922).

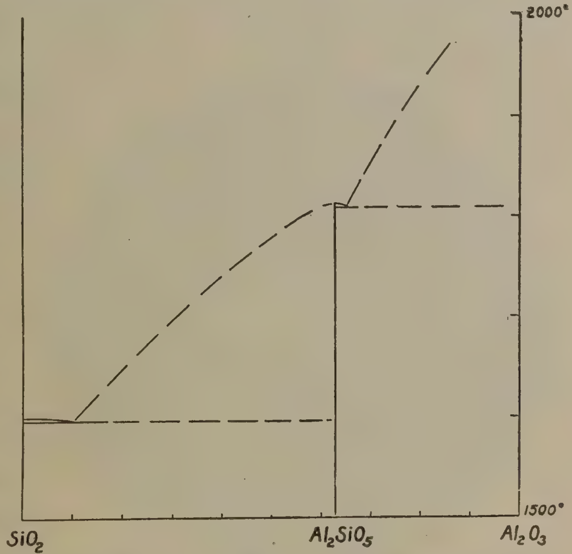

FIG. 2.—Equilibrium diagram of the system: $Al_2O_3.SiO_2$ after Shepherd, Rankin and Wright.

Preliminary trials with both natural sillimanite and with a mixture of Al_2O_3 and SiO_2 in the 1:1 ratio showed that, when they were heated to a very high temperature and slowly cooled, good corundum crystals were formed (see Fig. 3) showing that there is indeed a temperature region in which corundum exists in contact with liquid in a mixture of the composition of sillimanite. At the same time it was found that under no conditions that we were able to realize could the 1:1 mixture be induced to form a homogeneous mass consisting only of crystals corresponding with natural sillimanite. Even when not heated to the very high temperature where corundum forms, the mass always consists of two phases, the one, crystals having properties closely related to those of natural sillimanite; the other, interstitial glass. Precisely the same observation was made in the earlier work, Wright commenting as follows: "In every preparation of sillimanite examined there was present between the sillimanite fibers an isotropic substance of much lower refractive index, about 1.530. This same substance appears in other preparations of the alumina-silica series and is probably glass."[1] It was assumed in the earlier work that this was merely sillimanite glass that had failed to crystallize but we found that even when the mass was treated in such a manner that crystals several millimeters long were formed, the interstitial glass was as plainly present, in fact, was more definitely determinable as glass. Now it is contrary to all our experience with any compound which crystallizes readily enough to form large crystals that some of the compound should persistently retain the glassy condition. We were led to conclude, therefore, that the glass did not have the same composition as the crystals and, from its low refractive index and its refusal to crystallize, that it must be rather highly siliceous. If the glass is more siliceous than the total composition of the mass then the crystals must obviously be more aluminous. Acting on these indications we proceeded to determine the composition of the crystals by making up mixtures with more alumina than the 1:1 ratio. In accordance with our expectations it was found that with addition of alumina the amount of crystals increased and that of glass diminished until at the composition $3Al_2O_3.2SiO_2$ the glass had entirely disappeared and the whole preparation consisted of crystals identical with those in the 1:1 preparation. Unquestionably, then, these crystals have the composition $3Al_2O_3.2SiO_2$ and are not sillimanite at all, although they show a very remarkable similarity with sillimanite in optical and crystallographic properties, a fact which will be brought out more fully at a later point.

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[1] Shepherd, Rankin and Wright, *Am. J. Sci.*, **28**, 302(1909).

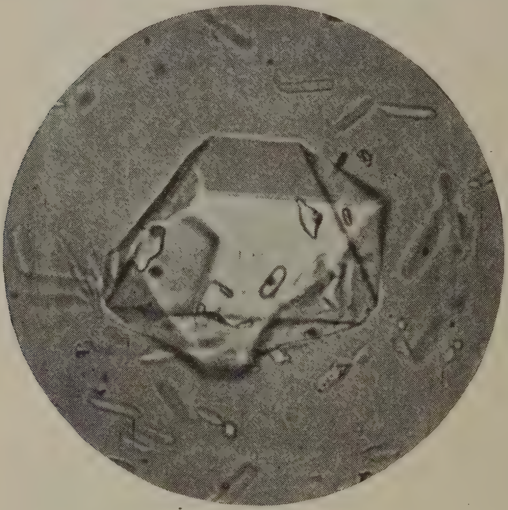

FIG. 3.—Corundum crystal (combination of base and rhombohedron) from preparation of composition $Al_2O_3.SiO_2$ cooled slowly from 1900 °C to 1810 °C and then quenched.

Method of Investigation

These preliminary observations showed that revision of existing concepts of the relations of alumina and silica at high temperatures was necessary. We, accordingly, proceeded to investigate systematically various mixtures covering the whole range of compositions. The method of quenching was adopted for the reason that it permits the determination of the phases present in any mixture at any temperature. For temperatures up to 1750°C we had the advantage over the earlier investigators of the use of a furnace wound with a wire of platinum 80%, rhodium 20%, constructed by our colleague, H. S. Roberts. In this furnace ordinary quenching experiments can be conducted under very favorable conditions and the temperature can be measured with a platinum-platinum rhodium thermocouple. For temperatures above 1750° an iridium tube furnace was used and the temperature measured optically. Such a furnace is not so well adapted for quenching work as could be desired but we found it possible to hold the temperature constant within a range of 8° to 10° and then to cool the charge rapidly by quick removal from the furnace. Charges with more than 50% alumina are usually not cooled rapidly enough to quench in the stricter sense of the term, but any new crystals formed during cooling are, in general, very minute as compared with the larger crystals formed during the period of constant temperature in the furnace and the two are thus distinguishable under the microscope. At its worst the method has distinct advantages over the method of observing the temperatures at which heat effects occur, for too often in such work the nature of the change of phase causing the heat effect can only be surmised.

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[1] Shepherd, Rankin and Wright, *op. cit.*, 325.

The thermocouple used to measure temperatures below the melting point of platinum was calibrated at the anorthite point and the platinum point. The optical pyrometer employed was a Leeds and Northrup equipment which had been calibrated by the Bureau of Standards. To obtain constancy of conditions in our own work we matched the filament against a disc of magnesia on which the iridium foil containing the charge rested. In each run a small piece of platinum was placed on the magnesia disc alongside the charge and its melting observed as the temperature was raised. Working thus we were able to duplicate the platinum point within ±5°. The small deviation from the standard value at this point was used as a correction to the standard curve.

The charges were made up from specially purified precipitated alumina and quartz. These were ground together in the desired proportion and heated at the highest temperature attainable in the Fletcher gas furnace, a temperature in the neighborhood of the melting point of platinum. The charge was then ground and returned to the furnace, heating with subsequent grinding being repeated five times. The microscope then showed the charge to be either a single homogeneous phase, or to have its constituent phases uniformly distributed. Samples of these charges were then used for the controlled runs in the iridium and platinum-rhodium furnaces.

Discussion of Equilibrium Diagram

The most noticeable feature of the equilibrium diagram, Fig. 4, is that $3Al_2O_3.2SiO_2$ is the only compound stable at these high temperatures. We have already presented our preliminary results fixing the composition of this compound, but the diagram serves to emphasize these findings. The $3Al_2O_3.2SiO_2$ preparation is a homogeneous aggregate of crystals of one kind at all temperatures up to 1810°C, where it begins to melt. A slight excess of alumina over the 3:2 ratio renders the charge inhomogeneous, corundum appearing in addition to the 3:2 compound. A slight excess of silica brings in a little cristobalite below 1545°C and a little glass (liquid) above that temperature. The 1:1 preparation, $Al_2O_3.SiO_2$, is in no respect unique but is like all those that contain an excess of silica over the 3:2 ratio. It consists of the 3:2 compound with cristobalite below the eutectic, 1545°, and of the same compound with liquid above 1545° (and below 1810°).

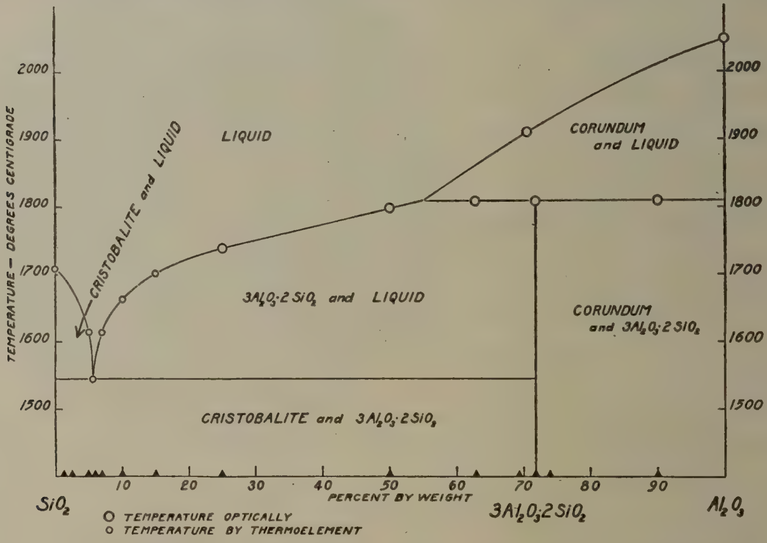

FIG. 4.—Equilibrium diagram of the system: $Al_2O_3.SiO_2$. After Shepherd, Rankin and Wright.

Only one eutectic occurs, that between $3Al_2O_3.2SiO_2$ and cristobalite. There is no eutectic between $3Al_2O_3.2SiO_2$ and corundum for the reason that the 3:2 compound melts incongruently, breaking up into corundum and liquid, at 1810°. Only when the temperature is raised to about 1920° does the corundum finally disappear and a mixture of the composition of the 3:2 compound is then completely molten.

The breaking-up of $3Al_2O_3.2SiO_2$ into corundum and liquid at 1810° is exhibited in all preparations extending over as far as those containing only 55% Al_2O_3. This range includes the 1:1 ratio (63% Al_2O_3) so that a mixture of that composition, while it consists as it approaches 1810° of liquid and crystals of $3Al_2O_3.2SiO_2$, experiences, at this temperature, an abrupt increase in the quantity of liquid accompanied by formation of a little corundum. It was this sudden formation of liquid that gave the heat effect at 1810° that was regarded in the earlier work as fixing the melting point of a 1:1 compound, and it was the same heat effect obtained in slightly more aluminous mixtures at the same temperature, that was regarded as the result of melting of the eutectic between a 1:1 compound and corundum.

TABLE I*a*

RESULTS OF RUNS IN PLATINUM-RHODIUM RESISTANCE FURNACE. TEMPERATURES MEASURED WITH THERMOELEMENT

Composition Weight per cent		Temperature, °C	Time, minutes	Result
Al_2O_3	SiO_2			
				Liquidus of Cristobalite
5	95	1611	50	Glass and cristobalite
5	95	1618	50	All glass
				Liquidus 1615° ±5°
				Eutectic—Composition and Temperature
5	95	1542	120	Crystalline
6	94	1542	120	Crystalline
7	93	1542	120	Crystalline
				Below eutectic
5	95	1546	40	Cristobalite and glass
6	94	1546	40	$3Al_2O_3.2SiO_2$ and glass
7	93	1546	40	$3Al_2O_3.2SiO_2$ and glass
				Above eutectic

Composition of eutectic $5^1/_2$% Al_2O_3; $94^1/_2$% SiO_2.
Temperature of eutectic 1545° ±5°.

Composition Weight per cent		Temperature, °C	Time, minutes	Result
Al_2O_3	SiO_2			
				Liquidus of $3Al_2O_3.2SiO_2$
7	93	1608	40	$3Al_2O_3.2SiO_2$ and glass
7	93	1614	40	Very rare crystals of $3Al_2O_3.2SiO_2$ in glass
				Liquidus 1615° ±5°
10	90	1663	60	Very rare crystals of $3Al_2O_3.2SiO_2$ in glass
10	90	1667	30	All glass
				Liquidus 1665° ±5°
15	85	1700	30	$3Al_2O_3.2SiO_2$ and glass
15	85	1703	30	Very rare crystals of $3Al_2O_3.2SiO_2$ in glass
				Liquidus 1705° ±5°

The Compound $3Al_2O_3.2SiO_2$[1]

Some excellent crystals of the $3Al_2O_3.2SiO_2$ compound have recently been prepared in the laboratory of the Corning Glass Works. After experiments in the fusion of alumina-silica mixtures in an arc, crystals were found protruding into pipes in the consolidated product. They were thought to be artificial sillimanite, $Al_2O_3.SiO_2$, but when they were brought to our attention we were able to state from the results of our work that crystals formed at such temperatures could be nothing but the $3Al_2O_3.2SiO_2$ compound. Analyses were accordingly made in the Corning Laboratory and the results bore out our prediction. The protruding crystals

TABLE I*b*

RESULTS OF RUNS IN IRIDIUM FURNACE. TEMPERATURE MEASURED WITH OPTICAL PYROMETER

Composition				Temperature, °C	Time, minutes	Result
Wt. per cent		Mol. ratio				
Al_2O_3	SiO_2	Al_2O_3	SiO_2			
Liquidus of $3Al_2O_3.2SiO_2$						
25	75	..	..	1753	6	All glass
25	75	..	..	1728	6	$3Al_2O_3.2SiO_2$ in large amount + glass Liquidus 1740° ±13°
50	50	..	..	1800	10	Rare crystals of $3Al_2O_3.2SiO_2$ in glass Liquidus 1800° ±10°
Temperature of the Invariant Point of $3Al_2O_3.2SiO_2$-Corundum-liquid						
62.9	37.1	1	1	1815	25	Glass + corundum
69.3	30.7	4	3	1817	3	$3Al_2O_3.2SiO_2$ + glass + corundum
71.8	28.2	3	2	1804	10	$3Al_2O_3.2SiO_2$
				1817	3	$3Al_2O_3.2SiO_2$ + glass
75	25	..	..	1803	5	Corundum + $3Al_2O_3.2SiO_2$ + very little glass
				1817	3	Corundum + glass
90	10	..	..	1804	10	$3Al_2O_3.2SiO_2$ + corundum. No glass
				1817	10	Corundum + $3Al_2O_3.2SiO_2$ + glass
Temperature of invariant point 1810° ±10°						
Liquidus of Corundum						
69.3	30.7	4	3	1912	12	All glass
71.8	28.2	3	2	1912	12	Corundum + glass At 1912° ±10° the liquidus lies between these compositions, *i. e.*, at 70.6% Al_2O_3 ±1.8%.

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[1] Since this paper was written we have discovered crystals of the $3Al_2O_3.2SiO_2$ compound in natural rocks from the Island of Mull. We propose the name *mullite* to designate the compound in a forthcoming paper in the *Journal of the Washington Academy of Sciences* where this natural occurrence of the mineral is described.

were broken off and thus obtained free from matrix or foreign material of any kind and therefore constitute particularly good material for analysis. The results, for which we are indebted to J. T. Littleton, Jr., are given in Table I.

TABLE II

ANALYSES OF CRYSTALS OF THE $3Al_2O_3.2SiO_2$ COMPOUND MADE IN LABORATORY OF THE CORNING GLASS WORKS

	I	II	$3Al_2O_3.2SiO_2$	$Al_2O_3.SiO_2$
SiO_2	27.60	27.35	28.2	37.1
Al_2O_3	73.16	72.87	71.8	62.9
TiO_2	none	none	..	..
Fe_2O_3	trace	trace	..	..
	100.76	100.22	100.0	100.0

Some of these crystals were very kindly turned over to us for examination. They are clear, transparent, colorless needles several millimeters long and upwards of a millimeter in diameter, with square cross-section but without terminal faces. Goniometric measurements on two crystals, A and B, gave the following results. (Table III.)

TABLE III

PRISM ANGLE OF CRYSTALS OF $3Al_2O_3.2SiO_2$

A	B	Mean	
90° 43′	90° 48′		
89° 13′	89° 22′	$110\wedge\bar{1}10$	$110\wedge 1\bar{1}0$
90° 52′	90° 46′	90° 47′	89° 13′
89° 10′	89° 06′		

The compound $3Al_2O_3.2SiO_2$ was prepared by Sainte-Claire Deville and Caron[1] as long ago as 1865. They passed SiF_4 over calcined alumina at a high temperature and obtained crystals which had the composition given under I and II, Table IV.

TABLE IV

ANALYSES OF THE $3Al_2O_3.2SiO_2$ COMPOUND BY EARLIER INVESTIGATORS

	I	II	III	IV	V	$3Al_2O_3.2SiO_2$
	Deville		Vernadsky	Cox		
SiO_2	29.1	29.5	29.7	30.07	28.89	28.2
Al_2O_3	70.9	70.2	70.3	69.93	71.11	71.8

Vernadsky in 1890 separated from Sèvres porcelain sillimanite-like crystals which proved on analysis to have the composition given under III,[2] Table IV.

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[1] *Ann. Chim. Phys.*, **5,** 114(1865).

[2] *Bull. Soc. Min. Fr.*, **13,** 270 (1890).

Recently Cox separated and analyzed crystals formed in a fire clay "exposed to a very high temperature for many weeks."[1] His results are given under IV and V, Table IV.

Vernadsky concluded that Deville's results and his own placed the composition of the crystals at $11Al_2O_3.8SiO_2$, and Cox accepts this conclusion for his own. It is true that all the analyses point to a composition of the material analyzed slightly more siliceous than $3Al_2O_3.2SiO_2$, though one of Cox's deviates very little in that direction. Nevertheless the material is in all cases such that it could scarcely fail to be contaminated in some degree with siliceous matter. Moreover, we have examined the crystals in various porcelain and fire-clay products and have also made some after the method of Deville and find that their refractive indices are identical with those of the pure $3Al_2O_3.2SiO_2$. We believe, therefore, that in all the cases the crystals have that composition.

The properties of the compound are remarkably constant, whatever the conditions under which it is made, so long as certain oxides which may be taken into solid solution are absent. No measurable variation of refractive indices can be detected in the crystals whether they are grown in a liquid containing 90% SiO_2, 10% Al_2O_3, or whether they are formed in the presence of excess corundum. Likewise there is no variation between crystals formed by sintering oxides at a comparatively low temperature or by fusing the mass in an electric arc. The properties of the compound are given in Table V below and compared with those of sillimanite from Delaware County, Pennsylvania.

TABLE V

PROPERTIES OF $3Al_2O_3.2SiO_2$ AND OF SILLIMANITE

		$3Al_2O_3.2SiO_2$	Sillimanite
Crystal system		Orthorhombic	Orthorhombic
Prism angle ($110 \wedge 1\bar{1}0$)		89° 13′	88° 15′
Cleavage		//010	//010
Optic orientation		$\grave{c} = \gamma$ and $\bar{b} = \alpha$	$\grave{c} = \gamma$ and $\bar{b} = \alpha$
Refractive indices	γ	1.654	1.677
	α	1.642	1.657
Axial angle	2V	+45°–50°	+25°

Natural Sillimanite

The mineral sillimanite, $Al_2O_3.SiO_2$, occurs in nature in crystals with a nearly square prism angle, with one cleavage diagonal to the prism to which the plane of the optic axes is parallel and the elongation is positive. In all these respects it is identical with the artificial $3Al_2O_3.2SiO_2$ compound. Only when precise quantitative measurements of optical and crystallographic constants are made can the two be distinguished and even then they are found to be very closely related. The detailed measurements of sillimanite from Delaware County, Pennsylvania are given in Table V, where they may be compared with those of $3Al_2O_3.2SiO_2$. Probably no other example is known of two distinct compounds of the same oxides that are so nearly alike in properties. So similar are they that, after having established the composition of our artificial compound beyond any possibility of question, we were led to doubt whether the composition of the natural mineral had been established. All the available analyses were old, so we selected very pure material which proved on examination under the microscope to be nearly free from foreign matter of any kind, and an analysis of this was kindly made for us by E. G. Zies of this laboratory. Our doubts were promptly dispelled, for the analysis, given below under I, Table VI, shows that the mineral undoubtedly corresponds with the 1:1 composition. After this analysis had been made another new analysis of a very pure sillimanite was published which shows a nearly identical composition (Table VI, II).

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[1] A. H. Cox, *Geol. Mag.*, Dec. 6, **5**, 61(1918).

TABLE VI

COMPOSITION OF NATURAL SILLIMANITE

	I	II	III
SiO_2	37.08	36.70	37.1
Al_2O_3	63.11	62.73	62.9
Fe_2O_3	0.09	.63	....
	100.28	100.06	100.0

I. Sillimanite from Delaware County, Pennsylvania, U. S. National Museum No. 9752, E. G. Zies, analyst. TiO_2 is less than 0.01%.

II. Sillimanite from Romaine, Quebec.[1] E. W. Todd, analyst.

III. Theoretical $Al_2O_3.SiO_2$.

These two excellent analyses confirm the accepted conclusion as to the composition of sillimanite and emphasize that it is a compound altogether distinct from $3Al_2O_3.2SiO_2$. It might be supposed that between two compounds so nearly identical in properties there would be a series of solid solutions intermediate in composition. If this were true there would also be a gradation of properties. However, the existing analyses of natural sillimanite never show a significant excess of alumina over the 1:1 ratio nor have we succeeded in preparing, in any iron-free mixture, crystals with properties that differ from those of the pure $3Al_2O_3.2SiO_2$ compound.

Behavior of Natural Sillimanite on Heating

While all the evidence shows that the 1:1 compound has no stable existence at high temperatures, nevertheless natural sillimanite can be heated for long periods at any temperature below 1545° without changing. We heated some for 6 days at 1350° but the microscope failed to reveal any evidence that it had begun to break up into the $3Al_2O_3.2SiO_2$ compound and free silica, which mixture of phases is shown by our results to represent the true equilibrium condition for this temperature. As soon as a temperature of 1545° (eutectic between $3Al_2O_3.2SiO_2$ and SiO_2) is passed, however, the sillimanite begins to be affected, forming crystals of $3Al_2O_3.$-$2SiO_2$ and a highly siliceous liquid (about 95% SiO_2). Above this temperature natural sillimanite behaves precisely like a 1:1 artificial mixture, that is, the liquid increases and the crystals of $3Al_2O_3.2SiO_2$ diminish in quantity until at 1810° there is an abrupt increase in the amount of liquid as a result of the break-up of the $3Al_2O_3.2SiO_2$ compound into corundum and liquid.

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[1] Walker and Parsons, Univ. of Toronto Studies, *Geol. Series* **16,** 36(1923).

At temperatures not far above the eutectic (1545°), crystals of natural sillimanite appear to change less readily than the 1:1 artificial mixture. This apparent difference is due to the contrasted structure of the two materials. The 1 : 1 mixture, even before being raised to a temperature above the eutectic, already consists of two phases, cristobalite and $3Al_2O_3.2SiO_2$, in random arrangement. When this aggregate is heated to a temperature above the eutectic the cristobalite disappears and the liquid formed constitutes a matrix for the minute prisms of $3Al_2O_3.2SiO_2$, still, of course, in random arrangement. This type of structure is well displayed in the photomicrograph, Fig. 5. On the other hand, natural sillimanite is a single, pure, crystalline phase and therefore perfectly homogeneous. Moreover the difference in crystal structure between sillimanite and $3Al_2O_3.2SiO_2$ is so slight that when liquid and crystals of $3Al_2O_3.2SiO_2$ are formed from sillimanite the new-formed crystals are coextensive with the original grains of sillimanite and of identical orientation. The liquid occurs as minute pellets and filaments in the large grains of $3Al_2O_3.2SiO_2$. The structure is shown in the photomicrograph, Fig. 6, which is to be compared with Fig. 5. Mechanically the aggregate formed from natural sillimanite is probably the stronger because the crystalline phase is the external phase, whereas the liquid phase is external in any synthetic 1:1 aggregate. At temperatures far above 1545°, however, where the amount of liquid is

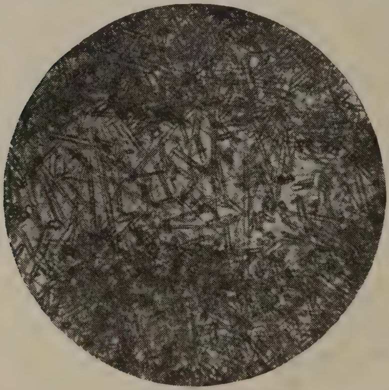

FIG. 5.—Photomicrograph showing structure of high-grade fire-clay cylinder heated at 1600°C–1700C° for several hours. Prismatic crystals of $3Al_2O_3.2SiO_2$ embedded in glass.

much increased, the difference between the two types of material is not so great but it is still noticeable at 1750°.

We thus see that natural sillimanite may, perhaps, have certain advantages over an artificial 1 : 1 mixture in a mechanical way; though not fundamentally any more refractory, but whether this difference observed in our small charges would be sustained in actual use under load our work does not enable us to state.

Alumina-Silica Refractories

The behavior of material containing alumina and silica in the 1 : 1 ratio has been discussed rather fully in the foregoing because it has hitherto been regarded as the most refractory mixture. We wish to emphasize, however, that the 1 : 1 proportion does not give the most refractory material. The $3Al_2O_3.2SiO_2$ mixture is far superior in this respect though it is equaled by any mixture with an excess of alumina over this proportion, all of which mixtures begin to melt only at 1810°C. The slightest excess of silica over $3Al_2O_3.2SiO_2$ is sufficient to cause a beginning of melting at 1545°C, the amount of liquid formed at any temperature being, of course, proportional to the amount of excess silica.

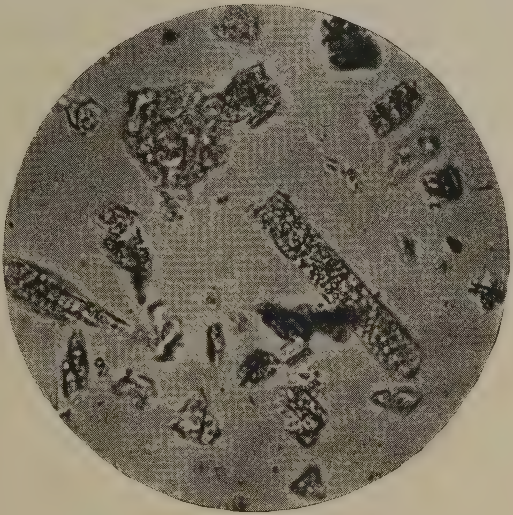

FIG. 6.—Photomicrograph showing structure of powdered natural sillimanite after heating at 1700° for 3 hours. Each grain of sillimanite, originally clear and transparent, is changed to crystalline $3Al_2O_3.2SiO_2$ in which are embedded pellets of a highly siliceous glass.

It is to be noted, however, that formation of some liquid at these relatively low temperatures may even be advantageous in some of the uses to which refractories are put. In the absence of other bonding material the liquid would serve as a bond which, by reason of its very high content of silica, is excessively viscous and, therefore, does not lead to ready deformation of the mass. Occurring at it does as the matrix of interlocking needle crystals of $3Al_2O_3.2SiO_2$, the material as a whole is quite strong unless the temperature is raised to such a point that the liquid is present in considerable amount, which temperature depends of course on the total composition and is highest for those compositions which approach $3Al_2O_3.2SiO_2$.

Moreover, the interstitial liquid ordinarily does not recrystallize on cooling but forms a glass which, since it is so highly siliceous, tends to endow the whole mass with the desirable characters of silica glass, principally resistance to fracture upon sudden heating and cooling. These remarks apply with special force to the pure alumina-silica mixtures. Where small amounts of alkalies, lime, magnesia, etc., are present all of these enter into the liquid which is very much increased in amount and loses much of its excellence as a glass because not so siliceous.

Broadly speaking, then, the refractory power of alumina-silica mixtures increases directly with the alumina content, omitting, of course, those mixtures with more than 95% silica. There is no maximum melting point anywhere in the series. To be sure all mixtures between SiO_2 and the compound begin to melt at the same temperature but the amount of liquid formed at any temperature decreases as the alumina content increases and becomes vanishingly small as the compound is approached, so the above generalization remains substantially true.

The compound itself, $3Al_2O_3.2SiO_2$, has very marked refractory power and it is noteworthy that one of the available analyses of Marquardt porcelain, that of an outer pyrometer tube, corresponds, barring its minor ingredients, fairly closely with the 3 : 2 compound, to which fact it no doubt owes its special refractory power. The analysis[1] is given below in Table VII.

TABLE VII

COMPOSITION OF REFRACTORY TUBE

	Pyrometer tube	$3Al_2O_3.2SiO_2$
SiO_2	29.75	28.2
Al_2O_3	66.52	71.8
Fe_2O_3	0.65	....
TiO_2	0.43	....
CaO	0.66	....
MgO	0.26	....
Na_2O	0.70	....
K_2O	0.92	....
H_2O	0.31	....
	100.20	100.00

It may be remarked here, too, that if natural sillimanite is to be used as a refractory the presence of some corundum in it, far from being detrimental, is a decided advantage.

Supposed Sillimanite in Various Wares

A great many investigators, including one of us, have regarded as sillimanite the needle-shaped crystals that form in so many kinds of ceramic wares and that resemble natural sillimanite to such a remarkable degree. We have examined materials in great variety, representing a wide range of compositions and treatments, including glass pots, tank blocks, special refractories, and "fused sillimanite." In all of these we have found the crystals to be $3Al_2O_3.2SiO_2$. In order to determine the crystals with certainty it is necessary to be able to measure the refractive indices. This presents some difficulty in the ordinary materials since they contain these crystals as minute needles completely surrounded by glass. However, by putting some of the powdered material in cold HF for a few hours the matrix is completely removed and the crystals can be transferred to immersion liquids for measurement of refractive indices. By careful handling, the refractive indices of the merest fibers can thus be measured. Working in this manner we found that in nearly every material we examined, whether it was a glass pot, "sillimanite" made by the Malinite process, "sillimanite" spark plugs or what not, the crystals have properties that do not differ significantly from those of pure $3Al_2O_3.2SiO_2$.[1] The first exception found was some material labeled "sillimanite from pot crowns" which we obtained through the kindness of Donald W. Ross of the Findlay Clay Pot Company. It was described as coming from the crowns of covered pots which had been in service for several months in commercial glass furnaces at temperatures from 1250° to 1450°. The crystals in this material were found to have the following indices, $\gamma = 1.672$ and $\alpha = 1.653$. These values are very much higher than those of $3Al_2O_3.2SiO_2$ and not very different from those of sillimanite. For a time in the early stages of our investigation we thought these crystals were sillimanite, $Al_2O_3.SiO_2$, but the failure of repeated attempts to make crys-

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[1] *Trans. Amer. Ceram. Soc.*, **15**, 607(1913).

TABLE VIII

CHEMICAL ANALYSIS OF CRYSTALS OF $3AL_2O_3.2SIO_2$

	I	II
SiO_2	29.36	28.2
Al_2O_3	69.05	71.8
Fe_2O_3	0.86	....
TiO_2	1.12	....
MgO	0.10	....
	100.49	100.0

I. Crystals from pot crowns. Analyst N. L. Bowen. Fe_2O_3 and TiO_2 by M. Aurousseau.

II. Theoretical $3Al_2O_3.2SiO_2$.

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[1] The porcelain of a recent type of Champion spark plug contains abundant crystals of corundum as well as of the 3:2 compound indicating a burning temperature within the corundum field. This is not necessarily above 1810°C for the presence of any foreign oxides that such material may contain would lower the temperature of the corundum field.

tals with such properties in pure alumina-silica mixtures led us to conclude that they owed their higher refractive indices to the presence of other oxides acquired from impurities in the clay. Accordingly we separated a quantity of these crystals from their matrix by means of cold HF, obtaining clean sharp crystals nearly free from matrix or foreign material of any kind. This material was analyzed with the results given in Table VIII. The crystals are plainly the 3:2 compound containing a considerable amount of iron and titanium in solid solution.

We thus encounter the very unfortunate complication that crystals of the 3:2 compound may have their properties changed in such a way that they are practically indistinguishable from sillimanite by optical means. To be sure, the indices of the pot crown crystals are still distinctly lower than those of natural sillimanite, but presumably $3Al_2O_3.2SiO_2$ crystals are capable of further contamination of the same sort and it would take but little more to give them maximum and minimum indices (and, of course, birefringence) indistinguishable from those of sillimanite. This fact is well brought out graphically in Fig. 7 where the curves of indices of iron-bearing $3Al_2O_3.2SiO_2$ crystals are shown. The curves have been extrapolated a short distance so that the end points correspond with the indices of hypothetical $3Al_2O_3.2SiO_2$ crystals containing somewhat less than 3% $Fe_2O_3 + TiO_2$. These end points also agree sensibly with the indices of natural sillimanite, $Al_2O_3.SiO_2$, from Delaware County, Pennsylvania, which contains only 0.09% Fe_2O_3 and practically no TiO_2.

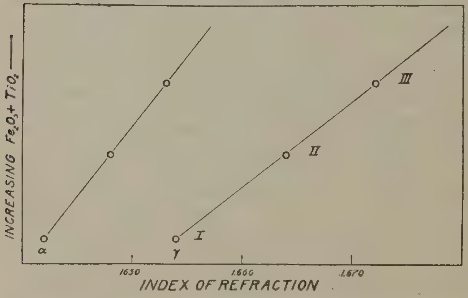

FIG. 7.—Curves of refractive indices of crystals of $3Al_2O_3.2SiO_2$ containing Fe_2O_3 and TiO_2. I, pure $3Al_2O_3.2SiO_2$, II, Eitel's crystals, III, pot crown crystals with 2 per cent $Fe_2O_3 + TiO_2$. Points at extrapolated terminations of curves agree very closely with indices of natural sillimanite from Delaware County, Pennsylvania.

We are able to place on this plot one other example of $3Al_2O_3.2SiO_2$ crystals. These were not obtained from ceramic ware but were prepared by Eitel by an alumino-thermic method and their properties recorded by him.[1] He regarded them as sillimanite, but crystals prepared in such a manner could be nothing but $3Al_2O_3.2SiO_2$. Their indices ($\gamma = 1.664$, $\alpha = 1.648$) are decidedly lower than those of sillimanite and somewhat higher than those of pure $3Al_2O_3.2SiO_2$, but both indices correspond well with those of crystals of this latter compound containing about 1% Fe_2O_3 ($+TiO_2$). Both iron and titanium were present in the raw materials and the fact that the crystals are pleochroic shows that a significant amount has entered into their make-up.

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[1] W. Eitel, *Z. anorg. Chem.*, **88**, 173 (1914).

We must emphasize again that this gradation of the properties of the $3Al_2O_3.2SiO_2$ crystals towards those of sillimanite is not due to any gradation of composition between these two compounds. Chemically, they are always distinct. Fortunately, too, the content of iron in the crystals formed in ceramic materials is, in the vast majority of cases, too small to lead to any confusion of these crystals with sillimanite if careful measurements are made.

It should be pointed out here that Vernadsky, whose preparation of $3Al_2O_3.2SiO_2$ we have already mentioned, also made material which he believed to be sillimanite by simple fusion together of alumina and silica.[1] Since our very numerous attempts to achieve this result cover the widest possible range of conditions we are thoroughly convinced that sillimanite cannot be prepared in such a manner and that the material prepared and analyzed by Vernadsky could not have consisted of homogeneous crystals of a single substance but must have been a mixture.

Sillimanite, according to our observations, does not form in any alumina-silica mixture at any temperature at which the crystals grow to a sufficient size to be determinable. Moreover, we have added various fluxes to alumina-silica mixtures in order to lower the temperature at which determinable crystals could be obtained and thus succeeded in growing such crystals at 1050°C, but they are always $3Al_2O_3.2SiO_2$. There is, no doubt, some temperature, presumably still lower, at which sillimanite is stable, for Nature has made it in abundance, but we have not succeeded in imitating her.

Nor have we found sillimanite in ceramic wares of any kind. The crystals in these are always $3Al_2O_3.2SiO_2$. This observation would seem to be in disagreement with the X-ray analysis of porcelain made by G. Shearer.[2] He subjected natural sillimanite and a piece of porcelain to such analysis using the powder method and obtained identical spectra. However, our colleague, Dr. Wyckoff, has kindly made similar powder photographs of our very pure sillimanite from Delaware County, Pennsylvania (analysis I, Table VI), and also of the clear, transparent, microscopically homogeneous crystals of $3Al_2O_3.2SiO_2$ (analyses, Table II), and has found that they give identical spectra. This is no place for a discussion of the significance of this observation. Suffice it to say here that the crystals contained in a ceramic ware cannot be established as sillimanite on the basis of X-ray analysis since this method fails to distinguish between that compound and $3Al_2O_3.2SiO_2$.

Summary

Corundum is frequently formed from shales and clays when these are attacked by natural magmas or by artificial melts such as glasses even when there is plenty of silica present to form sillimanite. This setting-free of alumina as corundum suggested that sillimanite itself must melt incongruently, breaking up into liquid and corundum. The older work on the system: alumina-silica indicated a maximum, congruent melting point of sillimanite, but this was not as definite as could be desired and a re-examination of the system was therefore undertaken.

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[1] *Bull. Soc. Min. Fr.*, **13**, 263(1890).

[2] *Trans. Ceram. Soc.*, **22**, 106(1923).

The present study has shown that there is only one compound of alumina and silica stable at high temperatures. This compound is chemically distinct from sillimanite, $Al_2O_3.SiO_2$, since it has the composition $3Al_2O_3.2SiO_2$, but its optical and crystallographic properties are very close to those of sillimanite. On account of this similarity of properties the crystals of the $3Al_2O_3.2SiO_2$ compound have been regarded as sillimanite in earlier work.

Since the only compound existing at high temperatures is the 3 : 2 compound, a synthetic mixture of the composition $Al_2O_3.SiO_2$ is always found to be inhomogeneous. As ordinarily obtained, by heating to a temperature of 1600° to 1700°C, it consists of crystals of $3Al_2O_3.2SiO_2$ and a highly siliceous glass.

Natural sillimanite though unstable at high temperatures, is very inert and suffers no change when heated for several days at any temperature below 1545°C, the temperature of the eutectic between cristobalite and $3Al_2O_3.2SiO_2$. Above this temperature sillimanite breaks up into crystals of $3Al_2O_3.2SiO_2$ and liquid.

The compound $3Al_2O_3.2SiO_2$ melts incongruently, breaking up at 1810°C into corundum and liquid. The field of corundum and liquid extends not only beyond the 3 : 2 compound but also beyond the composition of sillimanite so that if natural sillimanite or a synthetic mixture of the same composition are heated to a temperature slightly above 1810°C they form corundum and liquid.

The most refractory mixture of alumina and silica is not the 1 : 1 mixture as has been supposed hitherto, for such a mixture begins to show some formation of liquid at 1545°. A mixture of the composition $3Al_2O_3.2SiO_2$ is much more refractory since it begins to melt only at 1810°C.

The crystals of so-called sillimanite occurring in various kinds of ceramic wares are always crystals of the $3Al_2O_3.2SiO_2$ compound. In the presence of much Fe_2O_3 and TiO_2 the crystals may take these oxides into solid solution and their properties may then be changed in such a way that they are indistinguishable from sillimanite except by chemical analysis. Fortunately, in the vast majority of wares the amount of iron and titanium is small and the crystals of $3Al_2O_3.2SiO_2$ are readily identifiable as such by optical means alone.

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THE SIGNIFICANCE OF DRAFTS IN DOWN-DRAFT, COAL-FIRED KILNS[1]

By Ralph A. Sherman,[2] R. F. Lunger,[3] and W. E. Rice[4]

ABSTRACT

The fundamental laws of gas flow are applied to the movement of gases through down-draft kilns. Data on pressure conditions in four kilns are presented graphically. The cause of draft, the superiority of the down-draft over the up-draft kiln, the significance of stack draft, the relation of draft and excess air, features of kiln design, and the comparative merits of forced, induced and natural draft are discussed.

Introduction

Among the data taken during the course of the investigation of burning problems in the manufacture of refractories, conducted by the Bureau of Mines in coöperation with the Refractories Manufacturers Association, were pressure readings in the stack and at various points within the kiln on several of the kilns investigated. Although the readings were not taken for the purpose of determining the laws of the flow of gases in these kilns, they are sufficiently accurate to serve as a basis for a discussion of the significance of drafts in down-draft, coal-fired kilns.

The Cause of Drafts

Bricks are burned by passing hot gases formed by the combustion of a fuel, such as coal, through the mass of ware set in a kiln. To burn the coal, air must pass through the bed of fuel, the hot gases must overcome the resistance to their passage through the ware, and as the gases would be objectionable if discharged near the ground level, they must overcome the friction of the flues and a stack which discharges them at some height above the ground and surrounding structures.

Since gases move only from points of high to lower pressure it is necessary to establish a pressure difference between successive points along the path of the gases. The pressure difference may be established by several different means. A pressure greater than atmospheric may be established under the grates by means of a fan, or forced draft; a pressure less than atmospheric may be established in the kiln by means of a fan or steam jet in the stack forcing the gases out of the kiln, or induced draft; or the same condition may be obtained by the difference in the weights of the column of hot gases in the stack and of the column of cold air on the outside, or natural draft. The latter method, natural draft, was the method used on the four kilns studied in this investigation and is the method most commonly used on periodic kilns.

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[1] Published by permission of the Director, U. S. Bureau of Mines. Presented at Atlantic City Meeting, Feb., 1924.

[2] Assistant Physicist, Pittsburgh Experiment Station, U. S. Bureau of Mines.

[3] Junior Fuel Engineer, Pittsburgh Experiment Station, U. S. Bureau of Mines.

[4] Computer, Pittsburgh Experiment Station, U. S. Bureau of Mines.

Natural Draft.—The creation of pressure difference by natural draft may be illustrated from the sketches of Fig. 1. A and B represent columns of a light gas such as a kiln stack filled with hot flue gas and surrounded by air, A being open at the top and closed at the bottom and B closed at the top and open at the bottom. If W is the weight of the column of air over A above the level M-M, I is the weight of the gases inside the column A, and O is the weight of a column of air on the outside of the same dimensions as A, then the pressure on the inside at the level N-N will be $W + I$ and on the outside at that level $W + O$. Then the difference is $(W + O) - (W + I) = O - I$.

In the column B, closed at the top and open at the bottom, the pressure on the outside at the level M-M is W and on the inside is $W + (O - I)$ and the difference is $W + (O - I) - W = O - I$. Therefore, the total available pressure acting on a column of gas when at rest is equal to the difference in the weights of the column of gas and a column of air of the same dimensions, and the available pressure per unit area is equal to the difference in the weights of a column of gas and a column of air of unit cross-section and of the same height.

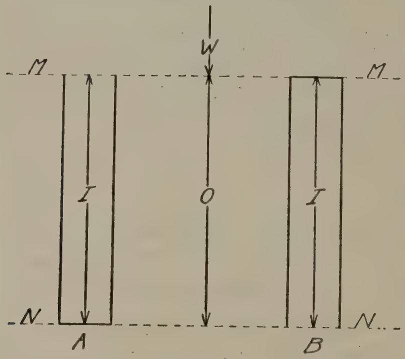

FIG. 1.—Cause of pressure difference between points within a column of light gas and the air outside.

As the density of a gas varies inversely as the absolute temperature the pressure difference will be greater, the greater the temperature difference between the hot gas and the air. Also, obviously, the pressure difference will be greater, the greater the height of the column.

If one leg of a U-tube filled with water be connected to a tube inserted into column A at the level N-N there will be a resultant difference in the water levels in the two legs equal to $0.192 \times (O - I)$ inch when O and I are expressed in pounds per square foot, 0.192 being the height of the water column in inches equal to a pressure of one pound per square foot.

It should be remembered that the reading obtained on a draft gage is the difference in the pressure of the gas inside and the air outside at the same level. It is immaterial whether the gage is placed above, at, or below this level, provided the temperature in the connecting tube equals that of the surrounding air. Thus, in B, Fig. 1, the pressure on the inside at the top M-M, $W + O - I$, is greater than the pressure at that level outside, W, but is less than the pressure at the bottom $W + O$.

When gage readings are taken at different levels, therefore, the pressure due to the weights of the columns between these levels must be considered.

Down-draft Versus Up-draft Kilns

The gases formed by the combustion of coal in the fire-boxes are divided by the ware into a great number of gas columns. Let us assume that the gases pass upward through these columns as in an up-draft kiln and that for some reason the ware in one column became hotter than in the others, then the gas in this column would give up less heat to the ware and would be hotter and hence lighter than the gases in the other columns and the force driving the gas through this column would become greater and greater as the temperature continued to increase. Conversely the temperature and pressure on the gas would tend to decrease in a column which had become cooled.

When the gases pass downward through the columns as in a down-draft kiln, if one column became hotter than others the force driving the gas down through this column would decrease and less gas would flow through this than through the other columns until the temperatures were equalized. Similarly, a greater force would act on a cool column until the temperatures were equalized. Thus, a much more uniform temperature may be secured in a down-draft than in an up-draft kiln.

Method of Reading Pressures

The pressure in the kilns and stack were read on a specially designed manometer connected by piping and rubber tubing to an open-end pipe inserted at the desired point at right angles to the probable path of the gas.

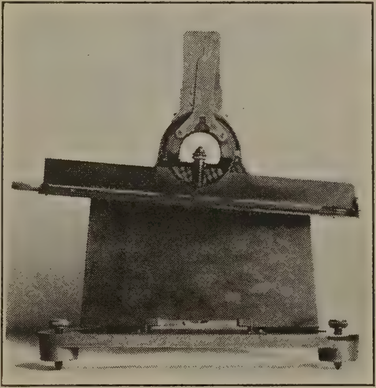

FIG. 2.—Inclined manometer.

The manometer which is shown in Fig. 2 consists essentially of a glass U-tube so mounted that it may be inclined to any desired angle in order that small differences in pressure may make a large difference in the reading of the manometer. Gasoline of specific gravity 0.715 (water = 1) is used in the gage to further increase its sensitivity. Scales used with the various angles of inclination are so calibrated that the readings are obtained directly in inches of water. At the smallest angle of inclination the instrument is sensitive to one one-thousandth of an inch of water.

Hourly readings were taken in the flue leading to the stack and at other points at approximately 4-hour intervals throughout the length of the burn. Readings were taken at the top of the kiln just inside the crown, inside the top and the bottom of the wicket and on some kilns in the ash-pit and in the furnace.

As the gases doubtless did not flow at all times at right angles to the pipe the pressure readings at times may have been higher or lower than the real static pressure. The pressure probably varied across any horizontal plane in the kiln and therefore the pressures read did not represent the average pressure across the kiln.

A much more accurate method of obtaining the true pressure reading is to use a pipe with a closed end with small openings, $^1/_{16}$ inch or less, drilled in diametrically opposite sides of the pipe, the pipe being so inserted that the plane through the openings is at right angles to the direction of the gas flow.

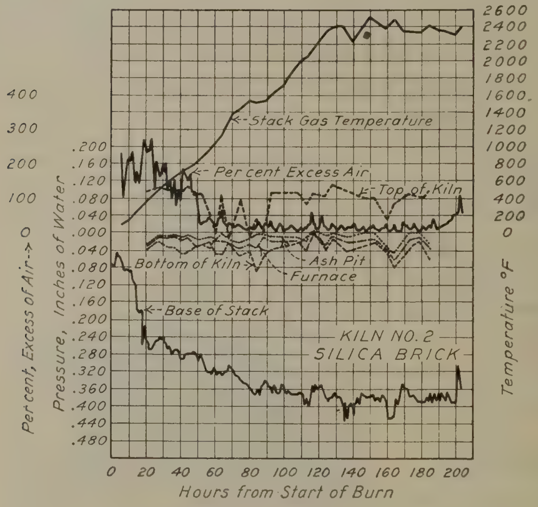

FIG. 3.—Variations in pressures at various points during burn.

The readings obtained on 4 kilns are plotted in Figs. 3, 4, 5, and 6 as ordinates, the hours from the beginning of the burn as abscissas. The stack gas temperatures and percentages of excess air in the gases are also shown. A sectional elevation of the kiln and a plan of the flue system is shown on each figure. The kilns are referred to as numbers 2, 5, 6, and 7, these being the numbers given the kilns in the investigation.

The pressure at the top of Kiln 2 was, with the exception of a few erratic readings, greater than that of the air at that level. The pressure in the ash-pit was generally less than that of the air at that level. If the difference in the pressure of the air at the two levels were not considered it would seem that gases were moving in the direction of a point of higher pressure.

This may be made clearer by a specific example. At the ninety-second hour in Fig. 3 the pressure in the ashpit was 0.008 inch of water less and at the top of the kiln the pressure was 0.092 inch greater than the pressure of the air at the respective levels. The temperature of the air was 75°F and that of the gases will be assumed to have been 2400°F. Assuming the gases inside the kiln to have the same density as the air at the same tem-

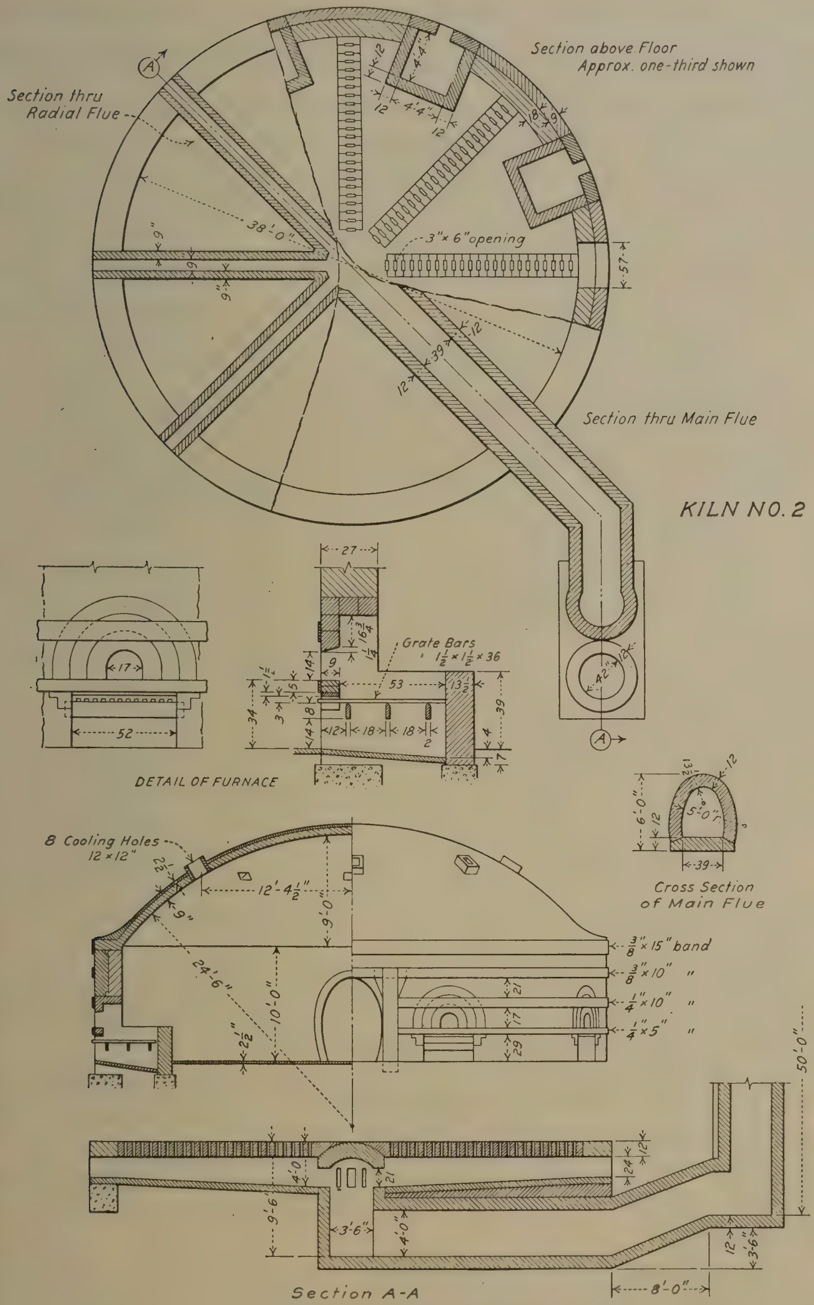
Section above Floor
Approx. one-third shown
Section thru Radial Flue
A
12
4'4"
12
4'4"
12
18
9
38'-0"
9"
9"
9"
3"×6" opening
57
12
39
12
Section thru Main Flue
KILN NO. 2
42"
12
A
27
16¾
1¼
Grate Bars
1½×1½×36
14
9
1½
5
53
13½
34
3
8
14
12
18
18
2
39
4
7
17
52
DETAIL OF FURNACE
13½
12
6'-0"
12
5'-0"
39
Cross Section of Main Flue
8 Cooling Holes 12×12"
22½
9"
12'-4½"
9'-0"
24'-6"
10'-0"
2½"
21
17
29
3/8"×15" band
3/8"×10" "
1/4"×10" "
1/4"×5" "
50'-0"
12
24
4'-0
21
9'-6
3'-6"
4'-0"
12
3'-6"
8'-0"
Section A-A

FIG. 3a.

perature and pressure,[1] the weight of the gases per unit volume at 2400° was $\frac{460 + 32}{460 + 2400} \times 0.0807 = 0.014$ pound per cubic foot, 0.0807 being the weight per cubic foot at 32°. In the same manner the weight of the air per cubic foot at 75° is found to be 0.074 pound. Then the pressure of the column of gases 14 feet high is $14 \times 0.014 = 0.196$ pound per square foot or $0.192 \times 0.196 = 0.038$ inch of water and of the air column of the same height $14 \times 0.074 = 1.036$ pounds or 0.199 inch of water. If p is the pressure of the air at the top of the kiln, then $p + 0.092$ is the pressure on the inside at the top and $p + 0.199 - 0.008$ is the pressure of the air in the ashpit. The actual difference in pressure between the ashpit and the top of the kiln is then $(p + 0.199 - 0.008) - (p + 0.092) = 0.099$ inch of water which is the force supporting the column of hot gases, giving the gases velocity and maintaining the velocity against the friction of the fuel bed. As the pressure of the hot gases has been calculated to be 0.038 inch of water the net pressure to overcome the friction of the fuel bed and walls and give the gas velocity was $0.099 - 0.038 = 0.061$ inch.

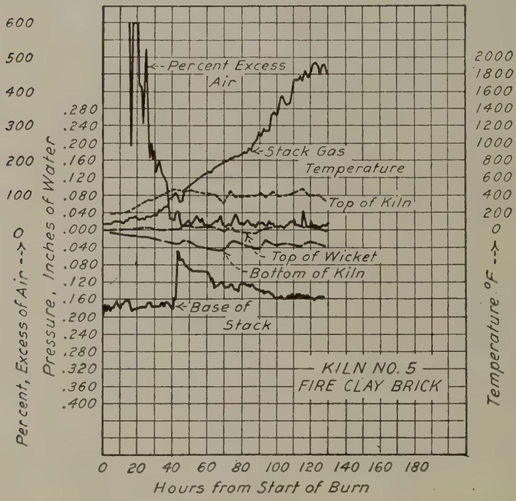

FIG. 4.—Variations in pressures at various points during burn.

This calculation is not exact owing to the probable inaccuracy of the assumptions. However, it is an example of the correction which must be applied to pressure readings taken at different levels.

The pressure in the bottom of the kiln was at all times less than that of the air. The depression in the stack increased due to increasing temperature of the gases to a maximum of 0.440 inch of water.

On Kiln 5 (Fig. 4), a fan was used in the stack up to about the fortieth hour which accounts for the decrease in the depression in the stack at that time.

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[1] This is obviously not correct as the density of the dry gases was probably 2 to 5% greater than that of the air. But as the gases also contain steam which is less dense than air any assumption as to the density would not be exact and no great error for the present purpose is introduced in assuming their densities to be the same.

In Kiln 6 (Fig. 5) the pressure at the top of the wicket was greater than atmospheric during practically the entire burn and the pressure in the bottom of the kiln was greater than atmospheric up to the fortieth hour. The stack was dampered several times toward the end of the burn.

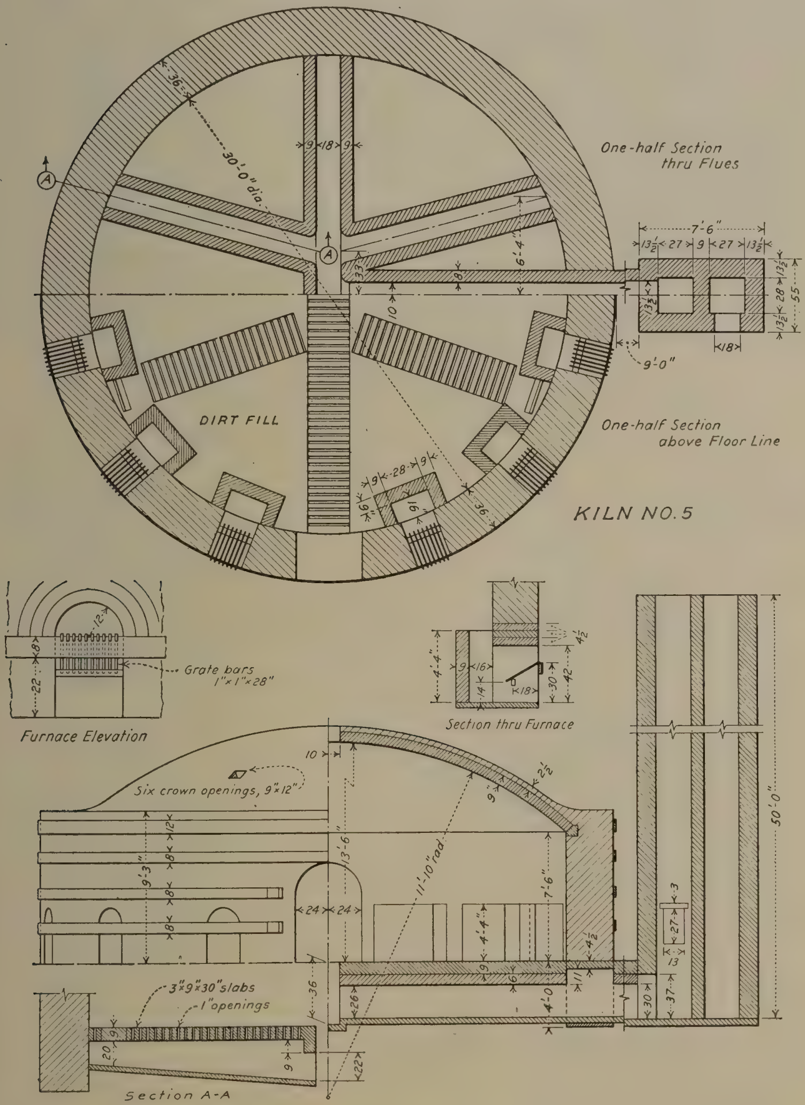

FIG. 4a.

The depression in the stack of Kiln 7 (Fig. 6), increased rapidly owing to the rapid rise in stack temperature. The pressure at the top of the wicket was less than atmospheric from about the thirtieth hour to the seventieth hour when the stack was dampered and the pressure in the bottom of the kiln was less than atmospheric throughout the burn.

Significance of Stack Draft

The maximum depression in the stack attained during the burn on 0.32 inch of water; and on Kiln 7, 0.34 inch. (See Figs. 3*a*, 4*a*, 5*a*, 6*a*.) These figures do not necessarily mean that more coal per square foot of grate area could be burned in the kiln with 0.44 inch depression than in the one with 0.20 inch depression in the stack. These values mean that there was this drop in pressure between the air at the grates and that point at the stack, assuming that these pressures were taken at the same levels.

The theoretical draft or pressure head on Kiln 2 measured on a gage at the base of the stack 53 feet high, if the ashpit opening and all other openings in the kiln were closed and the mean temperature in the stack were 1500°F, would be equal to

$$53 \times 0.192 \times 0.0807 \left[\frac{460 + 32}{460 + 75} - \frac{460 + 32}{460 + 1500}\right] = 0.546.$$

If the ashpit were opened and the gases allowed to flow the reading of the draft gage at the base of the stack would be less than 0.546 because a part of the total pressure head would be used to give the gases velocity and maintain that velocity against the frictional resistance of the stack.

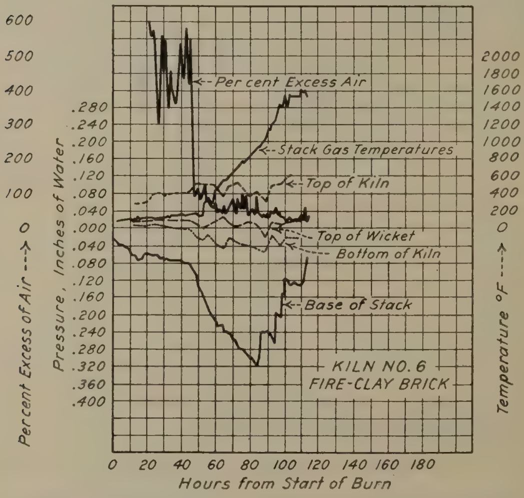

FIG. 5.—Variations in pressures at various points during burn.

At this time in this kiln the pressure read at the base of the stack was 0.360 inch and in the ashpit 0.008 inch of water less than atmospheric. Correcting for the difference of 9 feet in the two levels the true pressure drop between the two points is found to be 0.224 inch of water. If we had two kilns having exactly the same resistance or if in one kiln the resistance were constant then the depression in the stack would be a measure of the rate of flow of gases in the two kilns or at different times on one kiln, as the pressure drop varies as some power, about the square, of the velocity, or, pressure

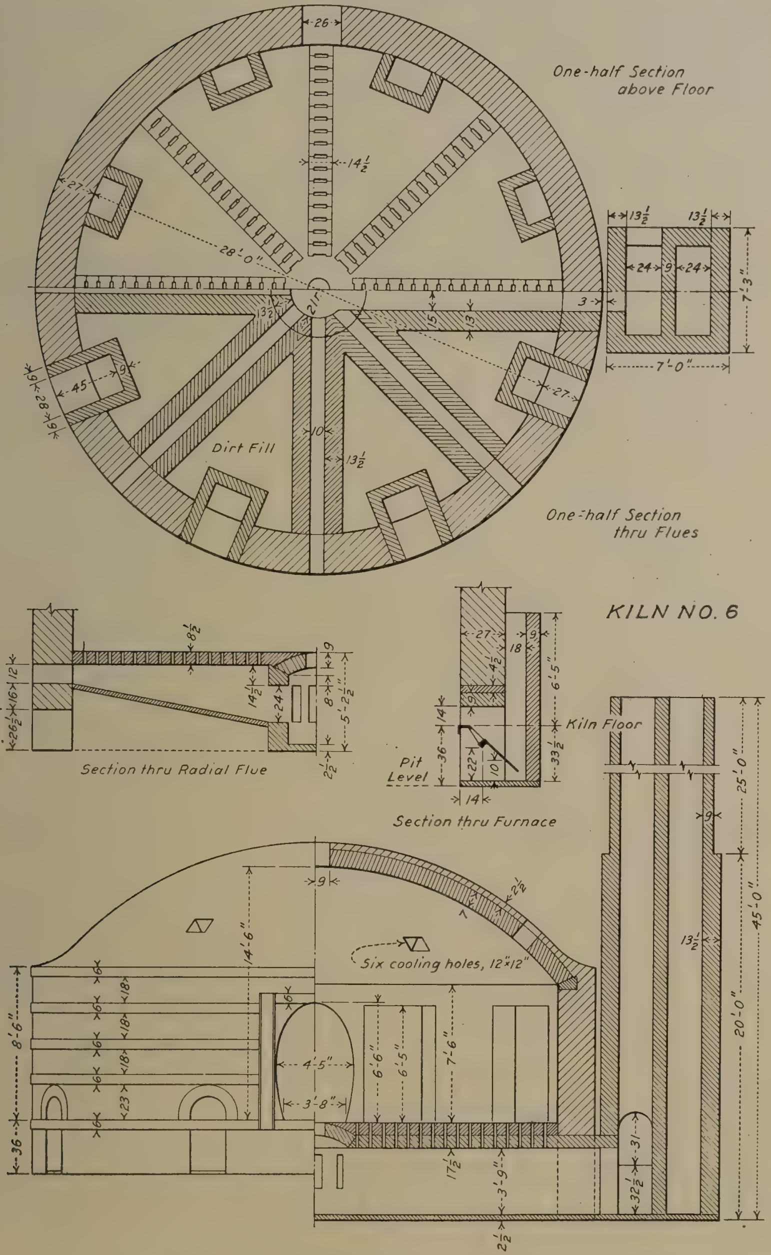
One-half Section above Floor
One-half Section thru Flues
KILN NO. 6
26
14½
27
28'-0"
21
13½
15
13
3
13½
13½
24
9
24
7'-3"
7'-0"
45
9
9
28
9
27
10
13½
Dirt Fill
Section thru Radial Flue
Pit Level
8½
12
16
26½
14½
24
9
8
5'-2½"
2½
Section thru Furnace
27
9
18
4½
6'-5"
Kiln Floor
14
36
22
10
33½
14
25'-0"
45'-0"
20'-0"
9
13½
Six cooling holes, 12"×12"
14'-6"
9
2½
8'-6"
6
18
6
18
6
18
6
23
6
36
6
4'-5"
3'-8"
6'-6"
6'-5"
7'-6"
17½
3'-9"
2½
31
32½

FIG. 5a.

drop = $K \times V^n$ where n is probably approximately 2. The constant K depends on the size and shape of the duct, the roughness of the walls, and on the density and viscosity of the gas which in turn are dependent on the temperature.

The resistance at a given velocity from the ashpit to the base of the stack is a sum of the resistance of the fuel bed which is a variable quantity, and the resistance of the walls, ware, and flues which are practically constant quantities though the resistance of flues may change owing to change in cross-section by accumulation of dust and ashes.

If, therefore, a true reading of the pressure in the bottom of the kiln could be obtained together with the temperature of the gases the pressure drop through the flues could be used as a measure of the rate of flow of the gases through the kiln.

At the time that the temperature of the stack gases was 1500°F in the kiln considered above, the pressure reading obtained in the flue to the stack was 0.360 inch, that in the bottom of the kiln was 0.040 inch and in the ashpit was 0.008 inch of water less than the air at the corresponding levels. Correcting these readings for the difference in the levels the pressure drop from the ashpit to the stack or the total drop through the kiln was 0.224 inch of water and the drop from the bottom of the kiln to the stack was 0.213 inch of water. Therefore, at this time about 95% of the total pressure drop through the kiln occurred in the flue system. Since the resistance of the fuel bed varies from time to time this percentage will vary.

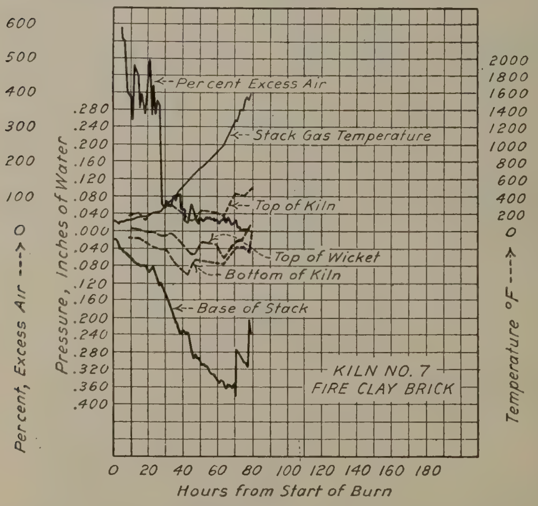

FIG. 6.—Variations in pressures at various points during burn.

A similar calculation at the time of maximum total drop for the other kilns shows that the pressure drop through the flues was approximately 65% of the total drop in Kiln 5, 80% for Kiln 6, and 74% for kiln 7.

The flue system, therefore, actually acts as a damper and it is evident that if the resistance of the flues were decreased the height of the stack could be decreased.

Actual Draft Required

Let us assume the gases in the kiln as moving through a duct as shown in Fig. 7 in the form of an inverted U in the direction A to D. When the grate is at the ground level the air pressures on the outside at each opening

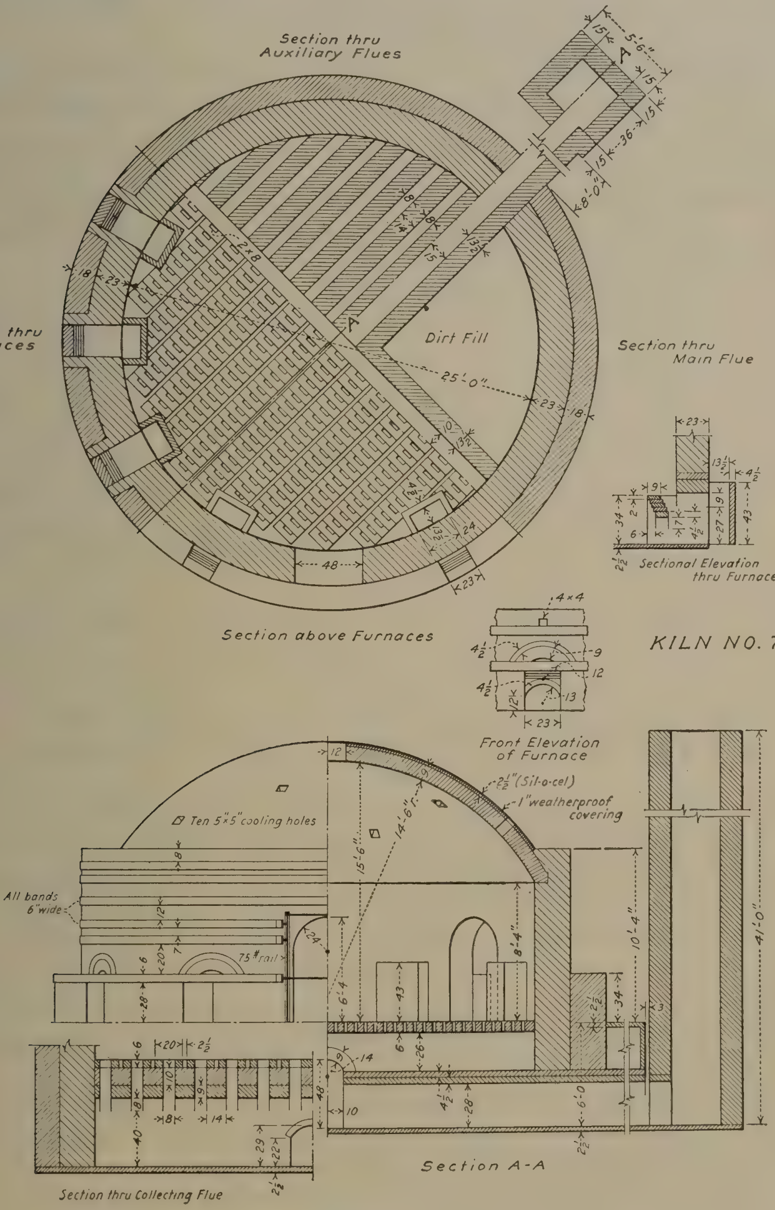

FIG. 6a.

of the duct are equal. Therefore, as the gases are cooler in the column *CD* than in *AB*, having given up heat to the ware, the weight of the column *CD* is greater than *AB* and the gases will flow out at *D*. If this difference is insufficient to draw the gases through at the desired rate, then the pressure at *D* must be decreased or that at *A* increased in order to move the gases. This may be done by a fan or by a stack.

If the grate level is moved to a point at A_1, above the floor level the pressure of the air at *D* will be greater than at A_1, by the weight of the column of air *A*, A_1. The difference in the weights of the two gas columns will be changed by the weight of the column of gas *A*, A_1. The change in the weights of the gas columns will be less than the change in the pressure of the air and hence the decrease in pressure at *D* or increase at *A* must be greater than before in order to move gas in the direction *A* to *D*. Similarly, if the grate level were moved to a point below the floor level the decrease at *D* or increase at *A* need be less than when at or above the floor level. Therefore, the resistance of the fuel bed and the walls being constant, the less is the distance of the grate above, or the greater below, the floor level the less is the depression or draft required at the bottom of the kiln in order to remove the gases from the kiln.

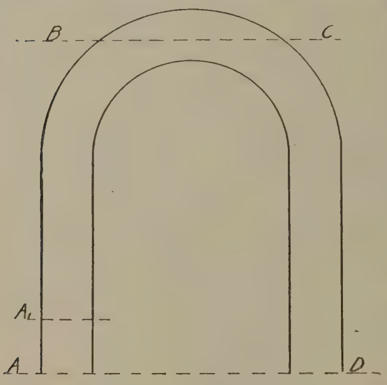

FIG. 7.—Imaginary duct representing path of gases through a kiln.

Obviously, the total pressure difference between the two columns depends on the height of the columns. The true height of the ascending column *AB* is difficult to determine. It is totally enclosed only by the bag-wall but as the ware is generally set around the bag-wall the true height is probably somewhat greater than the height of the bag-wall. It is possible that the pressure difference may be increased and the depression necessary at the bottom of the kiln decreased by increasing the height of the bag-wall.

The pressure difference between the two columns decreases as the burn progresses owing to the decreasing difference in the temperature of the gas in the columns. Thus, a greater depression is required at the bottom of the kiln which is, of course, produced by the increasing temperature of the stack gases.

The depression actually required at the bottom of a down-draft kiln, therefore, is small and the principal function of the high stack used on these kilns was to overcome the friction of the flues.

It has not been determined how the pressure drop from the bottom of the kiln to the stack is divided between the floor openings and the underground flues. The openings in the floor must be small and their resistance, therefore, fairly high in order to secure a uniform distribution of the gases over the floor. If the resistance of these small openings constitutes the greater part of the total resistance, the resistance cannot be greatly changed by change in the design of the floor opening and flues.

It has been seen from the charts of the pressure conditions in various parts of the kiln that the pressure near the top of the kilns was greater than atmospheric and that in Kiln 6 the pressure was greater than atmospheric in the bottom of the kiln during the first part of the burn. In this kiln, it is to be noted that the grate level was below the floor level of the kiln.

When the pressure inside the kiln is less than that outside, cold air will flow into the kiln through all openings, lowering the temperature of the gases and the ware. This is not especially harmful during the water smoking period but is detrimental later in the burn. Also, of course, when the pressure in the kiln is greater than that of the atmosphere, gases will escape from the kiln which may occasion a considerable loss of heat.

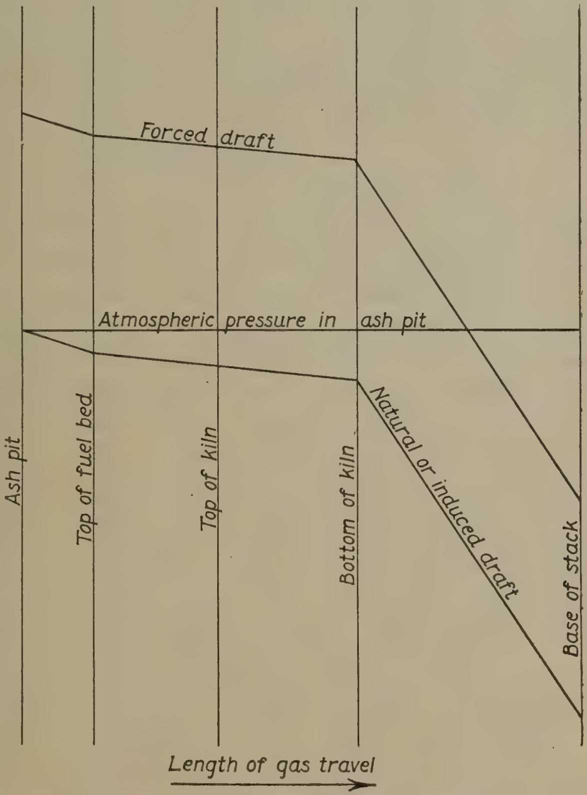

FIG. 8.—Approximate pressure drop through a kiln, using forced, natural or induced draft. assuming same resistance of fuel bed and kiln.

Therefore, the pressure within all parts of the kiln should be maintained as closely as possible at atmospheric pressure. Obviously, if the stack is dampered to reduce the depression the net force acting on the grate is decreased in the kiln and less coal may be burned. However, the temperature of the gases will be higher owing to the lessened infiltration of air and the temperature of the ware may often be raised faster with a dampered than with an undampered stack.

It has been pointed out that placing the grate level at, or below the floor level and increasing the height of the bag-wall will aid in maintaining the pressure in the kiln greater than atmospheric without decreasing the pressure head available to force air through the fuel bed.

When a kiln is lighted with a cold stack the available pressure head is very small. During the water smoking period it is desirable to force through the setting a large volume of gas at a moderate temperature. Several methods may be used to augment the small pressure head produced by the stack. The kiln may be operated as a semi-up-draft kiln by removing the covers from the cooling openings in the crown; a fire may be built in the stack or a fan may be attached to the stack.

Draft and Excess Air

Assuming that no free oxygen can pass through the fuel beds of a kiln the excess air present in the flue gases will vary directly as the ratio of the air admitted over the fuel bed, or secondary air, to the gases coming through the fuel bed. With a given area and depth of fuel bed and a given area of openings for air admission over the fuel bed the ratio of the pressure drop through the secondary air openings to the pressure drop through fuel bed and hence ratio of secondary air to fuel bed gases should remain constant with varying total pressure drop through the entire kiln.

Therefore, a change in the total drop through the kiln or the stack draft should have no effect on the amount of excess air in the flue gases, if the depth of fuel bed and openings over the fuel bed remain the same. It will be noted in Kilns 6 and 7 (Figs. 5 and 6) that the percentage of excess air decreased somewhat at the time the depression in the stack was decreased by dampering the stack. It may have been that at this time the firing openings were closed more tightly but assuming that they remained the same, the decrease in the percentage of excess air with a decrease in the depression in the stack may be explained as follows:

It has been pointed out that decreasing the stack draft increased the portion of the kiln in which the pressure was greater than that of the air outside. Therefore, some of the openings for secondary air admission were actually cut off and thus the ratio of secondary air to the fuel bed gases, and hence the percentage of excess air was actually decreased.

Forced and Induced Draft

It was pointed out in the introduction that the pressure difference necessary to move the gases through the kiln may be established in three ways: by forced, by induced, or by natural draft.

There is no essential difference in the movement of the gases by these three methods. That is, in order to move a given weight of gases through a kiln of given resistance the pressure drop through the kiln or through any part of the kiln must be the same regardless of the method used to secure the pressure drop.

Furthermore, aside from eddy currents which, at the low pressure differences considered, are probably negligible, the distribution of the gases will be the same with the three methods. Forced draft will not force gases into corners, nor will induced draft "pull" gases out of corners when used under the same conditions as natural draft.

Fig. 8 shows graphically the approximate pressure drop through a kiln with the three methods, the resistance of the kiln and the weight of gases moved being the same. Pressures at all points are with reference to the pressure of the atmosphere at the ashpit. As natural draft is but induced draft by natural means instead of by a fan the curves for induced and natural draft are identical. The pressure in the ashpit with forced draft is greater than atmospheric and as the pressure drop through the kiln is the same as for natural draft the curve lies above and parallel to the curve for natural draft at all points. Consequently a greater portion of the kiln will be at a pressure greater than the atmosphere and the detrimental infiltration of air will be less with forced than with natural or induced draft.

An obvious advantage of mechanical draft, either forced or induced, is the possibility of securing a greater pressure drop and thus moving a greater weight of gases than might be possible with natural draft.

Conclusions

The pressure readings taken at various points in these round, down-draft kilns showed:

1. That readings taken at different levels in a kiln must be corrected for the difference in the pressure of the atmosphere at these levels if the true resistance to the flow of gases through the system is desired.

2. The depression or draft in the base of the stack is not a true measure of the pressure available to force air through the fuel bed but is only an indication of the resistance of the kiln and flues. The pressure drop from the bottom of the kiln to the base of the stack, which measures the resistance of the flues was from 65 to 95% of the total pressure drop through the kiln in the four kilns studied. It is apparent that a design of a flue system having a lower resistance would be desirable, particularly during the water smoking period, when it is desired to force through the setting a large volume of gases at a moderate temperature at which time the depression produced by the stack is small. If the low resistance flue system permitted too great a depression at a later stage of the burn the stack could be dampered. This is dependent on, at present, the undetermined resistance of the floor openings.

3. It is desirable to maintain as great a portion of the kiln as possible

at a pressure slightly greater than atmospheric to prevent the infiltration of cold air. This condition is favored by placing the grate level at or below the floor level of the kiln, and also, perhaps, by increasing the height of the bag-wall.

4. There is no essential difference in the movement of gases by forced, induced, or natural draft. However, with forced draft a greater portion of the kiln may be maintained at a pressure greater than atmospheric.

Acknowledgments

NOTE: Acknowledgment is made of the helpful criticisms and suggestions o John Blizard, Research Engineer, Power Specialty Co., S. M. Kier, Kier Fire Brick Co., and M. D. Hersey, Physicist, Bureau of Mines. The data were taken by the crew of the laboratory car "Holmes," A. W. Whitford, A. H. Fessler, Franklin Wentzel, Jr., E. M. Rupp and W. T. Askin.

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DEVITRIFICATION IN A LIME-FLINT GLASS TANK[1]

By A. R. Payne

ABSTRACT

A brief account of the formation of cristobalite in a tank of soda-lime glass due to failure of the refractories in the bridge-wall. The efforts made to eliminate this devitrified glass are described. These efforts were not successful and the only solution was to shut the tank down and rebuild it.

The tank in which the devitrification occured has a melting end forty feet by twenty feet. Its refining end is twenty-two by twenty-eight feet and is roughly semicircular. Grouped about the refining end of the tank are eight presses, fed by flowspouts. The glass in the tank is forty-two inches deep. The bridge in the tank at that time was of the regular type being pierced by two holes for the flow of the glass and having a longitudinal passage for the air and water cooling system.

The glass being made was of the lime-flint type. An average analysis would be

SiO_2	73.23%
R_2O_3	0.56
CaO	4.54
MgO	3.43
Na_2O	18.24

The tank was started April 1, 1923. For four months the glass was normal. The average temperature in the melting end of the tank was about 2550°F, and in the refining end it was 2200–2250°.

About August 5, we began to get "dirty glass" from several of the flowspouts. This was intermittent and the scum was in small lumps. It was accompanied by cords. Invariably the "scum" crystals were in the cord. From that time on the glass was cordy on two or three shops continually.

The scum was not visible in the melting end of the tank. No batch piles ever got beyond the second port. Beyond that port the surface of the glass was as clean as a mirror.

When viewed through the flowspouts there was scarcely any scum visible in the refining end. It collected in the flowspouts, and adhered to the sides of the spout and to the plug. At times this scum was skimmed off the top of the glass in the flowspout and as a consequence there was less for several hours.

This dirty glass and cord occurred on certain shops only. The two corner shops always had good glass. The flowspouts where this scum emerged were not "cold." We tried heating them until the glass ran out like water with no benefit resulting. The glass then coming out was much too hot to be pressed, yet it was still cordy and contained this scum.

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[1] Presented at the Atlantic City Meeting, Feb., 1924. (Glass Division.)

At no time during this devitrification trouble was the glass seedy

We knew that the scum was not forming in the flowspout as the glass had been allowed to flow out extremely rapidly and the flowspout emptied itself in a very short time.

Composition of the Scum The scum samples were analyzed and were found to run high in silica. We pronounced the crystals to be cristobalite or tridymite. Samples were sent to Dr. Insley of the Bureau of Standards and he confirmed our ideas and pronounced them to be cristobalite.

A typical analysis of this scum was:

SiO_2	76.21
R_2O_3	0.82
CaO	3.82
MgO	2.90
Na_2O	16.25

This appeared to be the regular glass with some extra silica. When samples of the glass from each shop were taken and a composite analysis was made the results indicated that the batch entering the tank was normal and that we were getting every pound of every constituent that we were supposed to be getting. In all we made seven analyses of the glass from this tank.

Use of Alumina Knowing the advantages obtained by the presence of alumina we procured some aluminum hydrate and used 20 pounds per 1000 pounds sand for several days. This seemed to cut down the actual scum but did not improve the situation with respect to the cords.

Increase of Temperature We increased the temperature of the refining end to 2350–2375°, and in the melting end to 2600°F with no real improvement being shown.

Change in Batch With the idea that a stiffer glass might be less liable to crystallize in the danger zone (2200–1800°F), we decreased the quantity of soda ash in the batch. This change brought no betterment in the glass.

Conclusion

We were then of the opinion that we had exhausted our resources. It was decided that the crystallization was all occurring in the bridge and that batch changes and temperature changes were not sufficient to overcome the tendency of the glass to devitrify as it came in contact or near the water log in the bridge. We then had to choose between withdrawing the water log or shutting the tank down. It was a case where we had to choose between a continual fight against a slowly disintegrating bridge and a shutdown for quick repairs. We decided to shut the tank down. It was found that the glass had eaten the blocks in the bridge until it had exposed the water pipe. The glass surrounding the water pipe was completely devitrified and it was the continual sloughing away and the renewal of this mass of crystals that had been the source of our troubles.

HAZEL-ATLAS GLASS CO.
CLARKSBURG, W. VA.

COMBATING LAMINATIONS AND IMPROVING THE BRICK STRUCTURE[1]

By Davis Brown

Laminations are understood to be a succession of layers forming the rectangular structure of a brick and that the bonds between these layers are the weak points in the brick.

The causes of these laminations are fairly well understood but the remedy is a different matter.

The cause comes from a difference in the rate of travel of the material at different points under pressure, while undergoing change in size and shape necessary to convert the mass of material from a round to a rectangular section and to a reduced area. In undergoing this change it is necessary for the component parts of the structure to rearrange themselves in their relation to each other so that when the material issues from the die the structure is more or less laminated and of different densities at different points of its cross-section.

It is naturally of increased density near the corners or angles and of a lesser density at the center of the column where there is practically no resistance to its outward flow. In general, fatty clays laminate badly, the shrinkage is high and there is a tendency for the layers to separate during the drying and burning stages, being generally more pronounced at the latter period. Lean clays are not so susceptible and laminations do less harm owing to the fact, I believe, that the shrinkage is less.

The harmful effects of laminations are minimized by reducing them in whatever way possible. The most effective way is by reducing the plasticity of the clay, by adding grog or other suitable materials.

As regards the auger machine, there is evidently a proper ratio between the area of expressing cylinder and the area of the die but the requirements of the clay worker are so varied that it is difficult for the manufacturer of clay working machinery to cover them all.

Some fifteen or more years ago, when designing a new line of auger machines, I provided each machine with three sizes of expressing augers with sectional interchangeable bushings so the user could maintain the proper relation between diameter of auger and size of the die, which went a long way toward accomplishing the object in view.

All kinds of dies have been made but the choice has been pretty well narrowed down to three varieties and one or another of them is almost certain to give satisfactory results under favorable conditions.

The die should be kept as close to the auger as the material will permit as it saves power and wear and tear and the clay is not subjected to so much pressure. For the same reason, I believe in using as short a die as

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[1] Recd. Jan. 3, 1924. Presented at the Atlantic City Meeting, Feb., 1924. (Heavy Clay Products Division.)

the material will stand for as the more pressure required to force the clay through the die, the greater will be the difference in density between the center of the column and the outside.

At various times since about 1885, when I commenced to design clay working machinery, I, like many others, have had dreams of being able to overcome laminations, and have made many experiments with that end in view. In 1891, I built a roller machine in which a pair of rollers supplied pressure for forcing the clay through the die; installed one, as nearly as I recollect, at Stansberry, Mo., one at Cherokee, Iowa, one at Decatur, Ill., and one somewhere in Tennessee.

They all made a satisfactory brick with the exception of the one sent to Tennessee; the brick were somewhat laminated but in a different manner from those made on an auger machine and similar to those made on a plunger machine. The Tennessee machine was working a clay that was very fatty and when the customer sent a sample brick made on the machine it was apparent that the machine in question was not the solution of the difficulty and eventually all of them were replaced. What lead me astray was the fact that I did not procure a badly laminating clay for making the first trials.

The above experience cured me for a long time but of late years the dreams have recurred with so much persistency that I am at it again. This time the first trials were made with a clay which was giving serious trouble to the brick manufacturer. The brick would warp and check in the center and this difficulty was only minimized by mixing another clay, or grog, incurring much expense.

After working this clay successfully, I procured another of like characteristics and have succeeded in making samples of marketable brick from it.

At the present writing there are paving brick, fire brick and flux blocks made on this machine, undergoing physical tests and I am living in hope of being able to announce at an early date that the harmful effects of an imperfect brick structure need not be longer tolerated.

The plunger machine and the roller machine eliminate the "auger laminations" and retain "die laminations." The machine in question does not depend on an auger for creating the necessary pressure, nor a die for forming the column. It consists of three endless belts so arranged as to form a trough open at both ends and at the top. In this trough is a large roller located at the discharge end. The surfaces of all belts and the roller are driven at the same speed and in the same direction, where they are in contact with the clay. The space between belts forming the sides of the trough equals the length of a brick and the space between the roll and the belt which forms the bottom of the trough equals the width of the brick.

The prepared clay is fed into this trough behind the roll and issues in a column in the same manner as from any other brick machine but the column of clay is of uniform density; the brick do not warp and there are no weak spots anywhere.

On first going over this machine it would appear that as the material and moving parts in contact with it, travel at the same rate of speed, that it would be impossible to form laminations in the column issuing from the machine. This is borne out in practice so long as the supply of material is limited to that required to form the column free from voids and no more, as when an excessive amount of material approaches the point of greatest compression the excess material will flow backwards away from the roller and some laminations will appear in the column.

This is taken care of by means of a device for limiting the supply of material to the right amount. This device consists of an adjustable roller at the bottom of the hopper which once adjusted to the proper position for the material being used, permits the right amount to pass to the compressing roller, so long as material is kept in the hopper.

The main cause of weakness in a brick structure does not come so much from the laminations themselves as from the unequal density of the material at different points of the structure. The less dense portions shrink more than the dense portions, setting up stresses within the structure and reducing the strength of the brick.

In some of my demonstrations when using a laminating clay I have caused laminations to form in the column when supplying an excess amount of material yet the brick dried and burned safely and were straight and sound.

It is my ambition to be of service to the clay working industry and it is hoped that the presentation of this material will be of service in opening up a new line of thought or will prove of assistance in bringing about substantial advancement to that industry.

The Hadfield-Penfield Steel Co.
Bucyrus, Ohio.

THE EFFECT OF FURNACE ATMOSPHERE ON THE FIRING OF ENAMEL[1]

By R. D. Cooke

ABSTRACT

It is shown that in firing ground coat and other one coat enamels, the atmosphere of the furnace plays an important part. Oxygen in the muffle penetrates the enamel during the early stages of the firing forming a film of iron oxide on the surface of the steel. This film, whether applied before enameling or formed incidentally to firing, partially dissolves in the fused enamel giving the intimate bond between metal and enamel.

Ground coat enamel fired in an atmosphere of nitrogen was found not to adhere to the steel.

Approximate values are given for the proportion of furnace space to enameled surface to insure sufficient oxidation when residual air is depended upon to supply the oxygen.

It is the purpose of this paper to record a few fragmentary data on the firing of enamels rather than to be a complete study of the subject. The problem was encountered incidental to other work and was followed up from time to time as one observation suggested and led up to another.

While experimenting with melting small quantities of powdered ground coat frit on pieces of bare sheet steel, it was noticed that under the pile of frit the steel oxidized from the heat with nearly the same readiness as on the bare surfaces. This led to further experiments to determine whether the surface of the steel always oxidized from the heat when the ware was fired. It was found that it did. Ground coat biscuit ware was placed in a furnace a few seconds and withdrawn before the enamel had sintered. The enamel was washed off with water and it was found that the surface of the steel had become oxidized or blued. This observation is quite familiar to enamelers, but it is doubtful whether the full importance of the fact is realized.

Effect of Oxidized Versus Non-oxidized Iron in the Enamel

A number of small melts were made to show the effect of admixtures of iron and iron oxide to the enamel. A sample of dried ground coat enamel containing all of the mill additions was mixed with 20% of its weight of powdered iron scale and another sample with the same quantity of iron filings. These were melted by heating for five minutes at 900°C in covered porcelain crucibles. When cold the crucibles were broken and the interior of the melts examined. The melt with iron oxide was clear and quite free from bubbles, while the one with metallic iron was very spongy. This was another indication that in the proper firing of ground coat enamel the oxidation of the steel was more than incidental to the process; it appeared to be a vital necessity.

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[1] Presented at the Atlantic City Meeting, Feb., 1924. (Enamels Division.)

Equipment for Exact Studies

An electrically heated tube furnace (a laboratory carbon combustion furnace with silica tube) was so arranged that samples of bare or enameled steel could be introduced by resting them on a Monel metal boat, and pushing into the tube with a stiff wire. The opposite end of the tube was connected to a gas holder from which a current of any desired gas or mixture of gases could be maintained in the furnace.

Enameling Steel in Normal Atmosphere

Samples of clean steel were enameled with ground coat and fired in this furnace with a moderate current of air flowing. The enamel after firing was normal in every respect.

Enameling Steel in Atmosphere of Nitrogen

The atmosphere in the furnace was then changed to nitrogen and a number of pieces fired in the same way as before. The result was truly remarkable. The enamel had melted and rolled up into drops like water on a greasy surface, leaving areas of bright clean steel between. It adhered to the steel so poorly that most of the enamel could be rubbed off with the fingers.

Oxidizing the Steel before Enameling

Following this a number of pieces of clean steel were oxidized by heating for a few seconds at 750 °C and then enameled. These were fired in the atmosphere of nitrogen and came out as perfectly as those fired in air.

Summary of Evidence and Theory

Thus the fact was definitely established that the oxidation of the steel, by penetration of air through the porous enamel during firing, is a vital step in successful enameling. The true function of this oxide is not known, but a plausible hypothesis is that the film of oxide is dissolved in the enamel, at the higher temperature, forming a transition layer of composition varying from 100% enamel on the outside to 100% iron oxide next to the steel. The nitrogen experiment would seem to indicate that clean steel is not wet by fused enamel, while the enamel does wet iron oxide.

Reactions Involved in Firing Enamels

Equipment Used

The tube furnace was finally arranged to enable a more complete study to be made of the reactions involved in firing enamel. The silica tube extended several inches beyond the furnace at each end. At one end were connected a thermocouple extended into the heated zone, a manometer for observing the pressure in the tube, and a connection for gas or air supply. At the other end was an outlet for gases and device for pushing an enameled sample from the cold to the hot part of the tube, working through a stuffing box in order that the tube might be kept air tight while the sample was being fired and withdrawn. If desired the sample could be allowed to cool in the end of the tube before breaking the seals and removing it.

Samples The samples used were strips of steel three inches long and three-quarters of an inch wide bent lengthwise to a V-shape. The two edges rested on a Monel metal carrier. These samples were pickled and enameled in the regular way.

It was found that all pieces blistered badly when the air standing in the tube was depended upon to supply the oxygen. For normal results it was necessary to draw a slow current of air through the tube while the sample was being fired. About 100 cc. per minute was ample.

Effect of Pressure With these conditions as standard, samples were fired under reduced pressures by partially closing the air inlet. There was no bad effect from reducing the pressure to five inches below the barometer. This made it clear that variations in the barometric pressure could not effect the firing. All further experiments were made at atmospheric pressure.

Effect of Neutral and Slightly Oxidizing Atmospheres In an atmosphere of nitrogen the enamel blistered badly and collected in drops as before. In an atmosphere of carbon dioxide the enamel blistered but not as badly as in nitrogen. Pieces of bare steel heated in carbon dioxide oxidized slightly from reduction of the carbon dioxide to carbon monoxide, but the oxidation was not enough entirely to prevent the enamel from blistering.

Amount of Oxygen Required An effort was made to determine the quantity of oxygen taken up by the sample by analyzing the exhaust air from the tube. To avoid an unnecessary excess of air it was first necessary to determine the minimum rate of flow which would give good results. This was found to be 100 cc. per minute. When the rate was reduced to 90 cc. per minute the enamel blistered and spalled. To overcome the diluting effect of the large air spaces at the ends of the tube outside of the heated zone, the incoming air was carried through a capillary porcelain tube up to within an inch of the sample. The air was drawn out at the other end in the same way, the small porcelain tube being used to push the sample carrier into the furnace.

The average analysis of five samples of air collected in this way was: Carbon dioxide 0.7%, oxygen 16.5%. Since the original oxygen content of the air was 20.6% the amount absorbed was 4.1% of the total air passed. The rate of flow was 100 cc. per minute, and the sample was in the furnace one minute, therefore, the amount of oxygen absorbed was 4.1 cc. measured at room temperature. The total area of the sample was six square inches.

When Is Oxidation Effective? The oxygen was probably not being taken up throughout the firing period. This was shown to be true. A number of samples were fired with the air passing at the rate of 200 cc. per minute, and the samples left in the furnace exactly one minute. The air supply was cut off during different parts of the minute and the effect noted.

When the air was flowing the first thirty seconds and not during the last, the enamel was good. Under the reverse conditions, air flowing only during the last half minute, the enamel blistered.

When air was flowing only during the first quarter minute the enamel was bad, but when flowing only during the second quarter minute it was good.

The absorption period was narrowed down to the five-second interval between 15 and 20 seconds. For good results it was necessary that the air be flowing during that interval, which was presumably the interval just before the porous enamel fused to a continuous film.

If the 4.1% of oxygen absorbed were all taken up during that five seconds it is clear that for a moment the air surrounding the sample must have been entirely deprived of its oxygen.

Relation of Furnace Space to Area of Enameling Surface

In the practical firing of ware there is ordinarily no attempt at circulation of air in the muffle. The required oxygen must be found in the air standing in the furnace. The experiments thus far described failed to give any data which could be interpreted in terms of volume of furnace space required per square inch of enamel surface. The expedient was then tried of reducing the size of the samples fired in a fixed furnace space until the results were good. Strips of steel four inches long and $^3/_4$, $^1/_2$, $^1/_4$ and $^1/_8$ inch wide were enameled and fired in the tube furnace with no air flowing, but introducing fresh air into the furnace after each firing. It was found that the blistering or ruffling of the surface decreased with each decrease in the size of the sample until the $^1/_8$-inch strips were good. If it is assumed that the active furnace space extended one-half inch beyond the ends of the sample, the volume of the space was three cubic inches. The smallest sample had a surface area of one square inch. Since even this sample was not quite perfect it is safe to add at least 100% as a safety factor.

The conclusion is, therefore, that under the conditions of these experiments there should be for satisfactory firing six cubic inches of furnace space for each square inch of enamel surface.

It is admittedly taking a great deal for granted to assume that this conclusion can be applied to practical furnace conditions, mainly because there is nothing to show that air one foot from the enamel surface is as available as that within one inch. However, it is not without interest to compare this ratio with that found in practice in a number of typical instances. A number of items were chosen which off-hand appeared to have the greatest surface per furnace load. The surface areas were calculated from the weight of the ware and the known weight per square foot of the sheet steel. Two sizes each of coffee pots, tea kettles and milk kettles were figured. It was found that the cubic inches of furnace space per square inch of enamel surface varied from 9.8 to 14.1. The ratio of six to one is more likely low than high, and when it is seen that in practice the ratio may be as low as ten to one, it is obvious that the limit of safety may sometimes be passed.

The blistering mentioned in these paragraphs should be described as a very fine blister, appearing superficially as a mere dulling of the surface like very fine sandpaper. It was further observed that when the samples were drawn from the furnace and while still hot the surface was smooth and glossy. The blistering or ruffling occurred during cooling, and resembled somewhat the ruffling of the surface of molten paraffin wax when it solidifies. This effect was never seen when there was sufficient air in the furnace.

The experiments described above were performed on a ground coat enamel. All of them, however, were repeated on a one-coat gray enamel with identical results.

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Terra Haute, Ind.

OBSERVATIONS ON THE PROPERTIES OF CLAYS AND CLAY-GROG BODIES

By Edward Schramm

ABSTRACT

Determinations of shrinkage, absorption, and transverse strength were made on a series of clays and clay-grog bodies fired together. Highly porous grog bodies are obtained with tight burning clays when the latter possess high shrinkage. This is due to the formation of crevices between the clay and grog particles, and to produce a tight grog body the clay must be of low shrinkage and low porosity.

The data recorded below were obtained incidental to an investigation of sagger mixes and they are presented as a small contribution toward that much debated problem. The properties of a sagger mix or of any clay-grog body are determined by the nature of the clay, by the nature and grading of the grog, and by the kind of structure produced when the mixture of clay and grog is fired. To throw some light on the third factor, the interaction of clay and grog, the usual physical properties were determined for a number of clays and clay mixes and for the corresponding grog bodies with 50% of flint-clay grog. Two gradings of grog were used of the following analyses:

		A	B
Per cent rejection on	8-mesh	0	0
	14	1.7	31.7
	28	25.7	40.3
	48	33.0	19.8
	65	17.2	3.2
	100	3.0	1.7
Through	100	19.4	3.3
		100.0	100.0

The data on grog A briquettes is given in Table I, on grog B in Table II.

The tests recorded in Table I are of earlier date than those in II, and in the former case the strength of the fired clay was not determined. The briquettes were made by pressing in plaster molds. The clay was prepared by blunging into a slip, drying on plaster bats and careful wedging. In the case of grog mixes the grog was spread over the wet clay on the bat and thoroughly mixed in by wedging. All briquettes were first air dried and finished in an oven at 110°C. They were fired in the biscuit kiln bedded in kaolin. The measurements given are the average of four.

The figures, while not altogether consistent, enable us to trace certain general relationships between the properties of the clays and the clay-grog bodies made from them. The shrinkage of the grog mix is of course roughly proportional to that of the clay. With respect to absorption the relationship is not so simple. One might expect that the tighter burning clays would give a tighter grog body but this rule does not always hold. Thus in Table I we have two ball clays designated as Tennessee and Western and clay mix G which are vitrified or nearly so when fired alone and which yet give grog bodies of the highest porosity. On the other hand, in the same table we have the crucible clay of zero porosity giving the lowest porosity of any of the series of grog bodies. It will be noted, however, that the vitrified clays giving grog bodies of high porosity are characterized by high shrinkage while the crucible clay has a low shrink-

TABLE I

FIRED CONE 10

	CLAY BRIQUETTES			GROG BRIQUETTES					
Clay	Per cent shrinkage Drying	Per cent shrinkage Total	Per cent absorp.	Per cent shrinkage Drying	Per cent shrinkage Total	Per cent absorp.	Mod. rupt., lbs./sq. in.	Theoretical absorp.	Actual minus theoretical absorp.
Ky. Ball	4.25	12.25	0	3.9	7.0	11.8	2397	4.5	7.3
Crucible	5.00	10.75	0	3.2	6.0	9.6	2447	4.5	5.1
Tenn. Ball	4.75	14.50	0	4.0	8.5	15.3	2048	4.5	10.8
Mix B	3.75	12.00	7.2	3.2	6.2	13.4	2117	8.1	5.3
Mix A	5.00	12.12	4.1	3.2	6.3	12.4	2290	6.5	5.9
Mix D	4.37	11.25	1.8	3.8	7.0	12.5	2400	5.4	7.1
Mix E	5.62	11.25	0.8	4.0	7.0	12.7	2237	4.9	7.8
Mix G	3.75	14.37	1.3	4.0	9.0	14.4	2347	5.1	9.3
Mix I	3.75	11.25	3.0	3.0	6.8	12.8	2510	6.0	6.8
Mix J	4.00	11.25	6.3	3.5	6.2	12.7	2363	7.6	5.1
Western Ball	5.30	16.00	2.0	5.2	9.4	16.3	2200	5.5	10.8
Western Sagger	4.50	13.00	6.1	4.3	7.9	13.1	2627	7.5	5.6

TABLE II

FIRED CONE 11 HALF OVER

	CLAY BRIQUETTES				GROG BRIQUETTES					
Clay	Per cent shrinkage Drying	Per cent shrinkage Total	Per cent absorp.	Mod. rupt., lbs./sq. in.	Per cent shrinkage Drying	Per cent shrinkage Total	Per cent absorp.	Mod. rupt., lbs./sq. in.	Theoretical absorp.	Actual minus theoretical absorp.
Eng. China	4.0	10.1	20.8	3709	1.0	5.5	17.4	820	14.9	2.5
Fla. Kaolin	7.0	16.6	13.8	6420	3.6	8.1	16.3	1040	11.4	4.9
Tenn. Ball	6.0	14.6	0	6967	3.0	9.2	10.8	1572	4.5	6.3
Ky. Ball	6.0	14.0	5.4	5860	3.2	8.1	11.0	1780	7.2	3.8
Crucible	7.0	12.5	0.7	9937	3.0	7.2	9.1	1613	5.2	3.9
Ground Shale A	4.5	7.0	6.8	3366	2.0	5.5	9.4	1369	7.9	1.5
Ground Shale B	5.0	10.2	3.4	3341	2.0	6.0	9.4	1667	6.2	3.2
N. J. Fire-clay	5.0	14.0	12.9	....	3.0	8.2	15.0	1415	11.0	4.0
Eng. Ball	6.0	14.8	0	6580	4.0	8.9	9.9	995	4.5	5.4

age. It is evident that the shrinkage of the clay may be a factor of greater moment than its tightness in determining the porosity of a grog body.

In the series given in Table II we used a somewhat coarser grog and a greater variety of clays. At first glance the results do not appear so clear-cut but again we note that the Tennessee, Kentucky, and English ball clays of high shrinkage produce a more open grog body than the crucible clay or ground shales although the latter are more open in the clay state. On the other hand, when we are dealing with the very open burning clay such as the English china clay, Florida kaolin or New Jersey fire clay, it is apparent that the high porosity is due in part at least to the characteristics of the clay itself.

We may regard the porosity of a grog body as the sum of three components: (1) the porosity of the clay; (2) the porosity of the grog; (3) the pores and crevices which develop between clay and grog particles. We may calculate the porosity due to the first two factors from the known porosities of the clay and grog (9% absorption for flint clay). These values are entered in the table as theoretical absorption. The difference between the actual absorption and this theoretical absorption gives an idea of the extent of formation of crevices. It is the porosity due to these crevices which increases with increasing shrinkage of the clay and accounts for the highly porous bodies which may be obtained with vitrifying clays. The ideal clay for the production of a tight grog body is one which possesses both low shrinkage and low porosity.

The figures for modulus of rupture illustrate the well-known fact that the strength increases with decreasing size of grog. It is difficult to find any consistent relationship between the strength of the clay and clay-grog briquettes though it may be noted that the two ground shales exhibit the least falling off in strength when made into grog bodies. The bodies made from these clays also exhibit the smallest number of large crevices and the smallest differences between the actual and theoretical absorptions. The strength of a grog body is affected by the strength of the clay and of the grog, by the force of adhesion of clay to grog, by the number and distribution of cracks. The factors are so numerous as to make analysis impossible with any existing data.

ONONDAGA POTTERY CO., LABORATORY
SYRACUSE, N. Y.

ONE FIRE WHITEWARE AND ART WARE THROUGH DIRECT FIRED CAR TUNNEL KILN[1]

By A. E. Hull, Jr.

Introduction

The Harrop Car Tunnel Kiln recently installed at plant No. 2 of the A. E. Hull Pottery Co., Crooksville, Ohio, is most unique and interesting. This kiln was placed in operation in August, 1923, and is firing art ware, cooking ware, stoneware and whiteware with but a single firing. Each car setting is composed of these different kinds of ware—there being no distinction as to the location of the different kinds on the car. Practically a uniform burn is obtained over the entire setting. Ware is also fired open on top of the sagger bungs.

Size

The kiln is constructed with a side entrance vestibule at both the charging and discharging ends. The length from outside of vestibule to outside of vestibule is 307 feet. It accommodates 46 cars, 6 feet 7 inches long. The placing width is 4 feet 10 inches wide and the placing height 4 feet 10 inches.

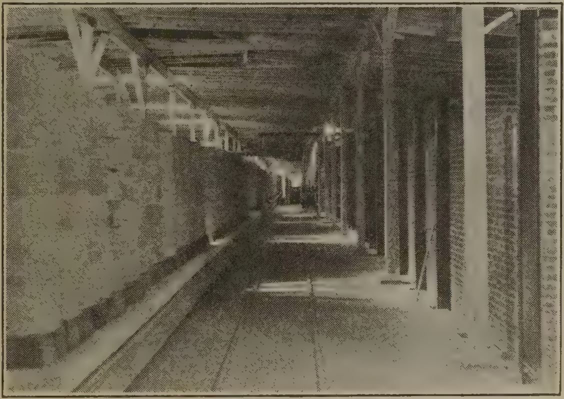

Fig. 1.

Capacity

The car setting contains an average of 435 pieces of ware.

The kiln delivers 31 cars of fired ware every 24 hours or 217 cars per week.

This gives an average production of 94,395 pieces of fired art ware, cooking ware, stoneware and whiteware per week, which is equivalent to the drawing of approximately five and one-half 30-foot diameter periodic kilns per week.

Time Schedule

Operating at a capacity of 31 cars per day requires the charging and discharging of a car every 46 minutes. This schedule requires but $35^1/_2$ hours for a car to travel entirely through the kiln. Sixteen and one-half hours are required to pass through the heating-up zone and three hours for the fire zone. This is a very large decrease in total firing time as compared to former periodic kiln practice in this plant. Although operating at a fast time schedule, the temperature at the charging end of the kiln is but 180°F and the temperature at the discharging end is only 170°F.

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[1] Presented at the Atlantic City Meeting, Feb., 1924. (Whitewares Division.)

There are four furnaces on each side of the kiln, although only three on each side are being fired. Highly oxidizing conditions are maintained throughout the kiln at all times.

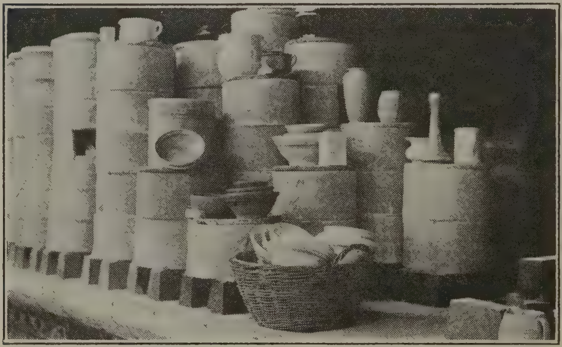

FIG. 2.

Operation of the Kiln

Due to the design and layout of the kiln, the operation is ideal. One man on each shift fires the kiln, maintaining the temperature, attending to the charging of the cars and taking the fired cars from the discharging end.

After a kiln car is pushed on the charging end transfer car, which in turn is placed in the charging end vestibule, an oil hydraulic car ram pushes the kiln car from the transfer car, moving the entire train of cars through the kiln at the rate of 1.7 inches per minute. The forward movement of the train delivers one kiln car onto the transfer car in the discharging end vestibule for every car introduced at the charging end. When the kiln car is entirely on this transfer car, both are removed from the

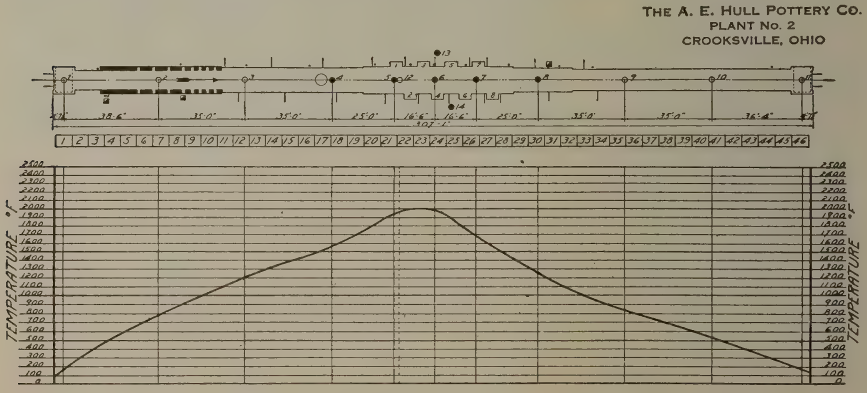

FIG. 3.—Temperature record, Harrop car tunnel kiln No. 1.

vestibule and the kiln car is placed on the return track. This latter track is completely filled with kiln cars, which are moved by a second hydraulic ram at the same rate as the train of cars in the kiln. This movement, being slow, is not objectionable to the kilnmen in placing and drawing the ware. It is so much easier to place and draw ware on a tunnel kiln car, where the sagger bungs are not high, that the kilnmen, without exception, say that they never want to work in periodic kilns again.

It is interesting to note that the total force required to move the train of cars in the kiln is 8300 pounds, while the force required to move the train of cars on the return track is 8000 pounds, there being but 300 pounds difference.

The kiln is equipped with Maxon Premix gas burners which are controlled by needle valves, thus requiring but little attention for regulation.

Advantages

The installation of this kiln has done a great many things for the A. E. Hull Pottery Co. We are obtaining a more uniformly fired product with a larger percentage of number one ware. In operating, placing and drawing, there is a labor saving of about 40% over our former periodic kiln practice, and there is also a fuel saving of about 85% over our periodic kiln practice. Due to the fact that the firing time is faster than in the periodic kilns and it being possible to single-fire the ware, production is speeded up considerably.

Last but not least, only about one-third of the number of saggers used in the periodic kilns are necessary with the tunnel kiln to obtain the same production. Furthermore, the actual saving in sagger breakage is approximately 25%.

A. E. HULL POTTERY CO.
CROOKSVILLE, OHIO

THE ELECTRIC BRASS FURNACE REFRACTORY SITUATION[1]

By H. W. Gillett[2] and E. L. Mack[3]

ABSTRACT

The three prominent types of electric brass furnaces are described, and the conditions which they impose on the refractories are outlined. The limitations which the properties of refractories place on the applicability of the various furnaces are considered and an attempt made to point out lines along which development and improvement are most likely to take place.

Introduction

The makers of electric brass furnaces admit that there is a refractory problem in the application of induction furnaces to alloys high in copper. Outside of that, each maker seems to feel that while the other furnaces have their unsolved refractory problems, he has his own well in hand.

Such service reports as the refractory maker gets are usually of conflicting natures, although reports of short refractory lives seldom fail to reach him promptly. Consequently the situation does not seem entirely clear to him, but, on the whole, he is inclined to believe that his materials give reasonably good service.

The furnace user thinks of the problem in terms of dollars and cents per ton of metal melted and, while he generally finds his over-all costs are very satisfactory with the electric furnace in comparison with fuel-fired furnaces, yet would like to whittle down his costs a little more by getting longer service from his linings before replacement. The user sees the problem as a rather larger one than any of the other interested parties, and is often at a loss to know whether he is using the best lining for his job or getting as good results from it as he should expect. He generally gets some guidance from the furnace maker who is in touch with many installations but is not always inclined to accept the furnace maker's view-point as entirely unbiased. The user will probably welcome an airing of the subject—the refractory maker and furnace maker may or may not.

The least satisfactory spot in the situation is the induction furnace for high copper alloys, but the other furnaces have problems almost as interesting.

One of the writers discussed the "Metallurgical Requirement of Refractories for Furnaces Melting Copper Alloys" in a paper before the American Ceramic Society last year,[4] but it will be necessary to go over again some of the ground covered in that paper in order to make the present situation clear.

Types of Furnaces

There are three main types of electric brass furnaces: the granular resistor (Baily), the moving indirect arc (Detroit and Booth) and the induction (Ajax and G. E.). Each has some refractory problems common to all types, but each also has some special problems of its own, and it is simpler to take each type up separately.

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[1] Published by permission of the Director of the U. S. Bureau of Mines. Presented at the Atlantic City Meeting. (Refractories Division.)

[2] Chief Alloy Chemist, Ithaca, N. Y.

[3] Assistant Alloy Chemist.

[4] H. W. Gillett, *Jour. Amer. Ceram. Soc.*, **6** [4], 596(1923).

Granular Resistor The Baily furnace, Figs. 1 and 2,[1] operates with a granular carbon resistor in a carborundum trough as the source of heat. Granular resistors are prone to develop hot spots, and it is necessary to run the resistor at such a high temperature that carborundum is the only available refractory that will stand up, and there actually is but a very small margin between the necessary resistor temperature and the decomposition point of carborundum. The trough is the weakest part of the furnace and in the past the furnace has been operated at a low rate of power input so as to avoid damaging the trough. This has resulted in low efficiency, small production, and a power cost per ton of metal melted which has made it difficult to compete with other more efficient electric furnaces, although it has in many cases shown decided savings over melting by fuel.

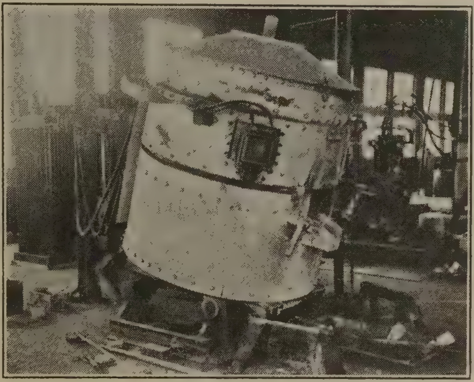

Fig. 3.—New form of Baily furnace.

But in the last two years this type of furnace has scarcely held its own, new installations hardly balancing old ones given up for one reason or another. There are some conditions where this type has advantages, and in the early days of electric brass melting it had more installations than any other. But, because of its low efficiency it now seems to be meeting with less favor. Moreover, another low efficiency furnace, the General Electric smothered arc furnace, which was handicapped in much the same manner as the Baily, has passed into "innocuous desuetude."

Some observers of the Baily furnace feel that the trough difficulties attending the use of higher power and hence higher trough temperatures are so great that this obvious method of increasing the efficiency cannot be satisfactorily used, and the furnace is still on the market in its original form. Mr. Baily is manufacturing a new form of this furnace (Fig. 3), in which he plans to increase the power input very greatly. He contemplates using up to 300 kw. on the furnace that formerly used only about 105.

[1] For Figs. 1 and 2 see *Jour. Amer. Ceram. Soc.*, **6** [4], 600, 601(1923).

Obviously, such a step will improve the efficiency markedly, and will equally obviously increase the refractory difficulties many fold. Recognizing this, the design of the new furnace, instead of supporting the trough on piers extending up from the hearth, supports it in a removable section just above the hearth, so that when the trough fails a spare section can be put in without long delay. The roof also is separate and replaceable. The hearth in the new type should show much the same life as in the old. The trough difficulties will be vastly increased and roof troubles somewhat. The new type has not yet been in operation long enough to secure quantitative data on refractory life, but the new design shows that refractory problems are expected to come up. The success or failure of the new type depends primarily on refractory performance.

The refractory life of the old type, run at low power input (105 kw.), was fair. The rammed hearth, of Corundite or of carborundum fire sand and fire clay or other refractories suitable for the purpose often melted 500 tons, but most hearths were torn out after smaller tonnages because the resistor trough had to be replaced more often and the users generally relined the hearth as well while the furnace was down. Such rammed hearths show some tendency to "float" and hearths built up as solidly as possible from brick appear to have given better results than the rammed ones.

The troughs gave from 125 to 500 tons, averaging perhaps 375 tons in the 105 kw. furnace. The Corundite or silica brick piers supporting the trough were sometimes injured in charging or by poking and some of the poorer results were due to such accidents.

The walls and roof, usually of Corundite, generally outlast several troughs. The Corundite is backed up by Sil-O-Cel.

In the early days the trough was rammed up in place, and such troughs often gave very short lives. The use of preformed sections remedied this considerably.

One user melting aluminum bronze in such a furnace, has used a hearth made up of ground fire brick, corundite clay and aluminum borings. The oxidation of the borings sinters the hearth together. 750 to 1000 tons has been obtained on such a hearth. The alloys melted contain aluminum, so a trace of that metal picked up from the hearth would do no harm, but such an expedient would be dangerous were the furnace required to melt the many types of brass, etc., in which the presence of small amounts of aluminum is fatal.

Moving Indirect Arc Type The moving indirect arc type (Figs. 4 and 5)[1] has no weak spot in the refractories corresponding to the trough of the resistor type, but since the furnace oscillates or rotates, the lining is all hearth, and the problem of penetration by metal is an important one.

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[1] *Jour. Amer. Ceram. Soc.*, **6** [4], 602, 603(1923).

Most of these furnaces are lined with fire brick high in alumina, Corundite being the usual choice, with Suprafrax also common. The Booth furnace has used a fire clay or Suprafrax lining with the whole cylindrical drum in one piece, for the smaller furnaces or two pieces for the one ton, furnace, with single pieces for each end, making a 3 or 4 piece lining. In the 250- and 500-pound sizes this is said to give about 125 and 250 tons, respectively, but some of the earlier users found the three piece lining decidedly unsatisfactory. Present opinion seems to be that these special linings do not stand up as well as brick in the larger furnaces, *i. e.*, over 500 pounds, and probably no better in the smaller ones, but they save some time in relining.

The Detroit furnace uses high alumina brick as standard, usually Corundite, sometimes Suprafrax. The furnaces have a Sil-O-Cel layer on the outside, and the larger ones usually have an intermediate layer of fire brick chosen for heat insulation rather than refractoriness. The intermediate layer is dispensed with in the 250-pound furnace. Although the power input is greater in respect to furnace volume and to weight of charge in the small furnace, the $4^1/_2$ inch Corundite lining backed up by $^1/_2$ inch asbestos cement and $1^1/_2$ inches of Sil-O-Cel appears to give as good or better life in heats than the $4^1/_2$ inch Corundite backed by $4^1/_2$ inch fire brick and $2^1/_4$ inch Sil-O-Cel in the larger furnaces. In 9-hour or "daylight" service, the efficiency of the small furnace, probably due to the smaller heat storage in the thinner lining, is almost up to that of the one-ton furnace. Some sizes use $6^1/_2$ inch Corundite, $^1/_2$ inch asbestos cement (to prevent metal that may penetrate the inner lining from getting into the Sil-O-Cel) and $4^1/_2$ inch bonded Sil-O-Cel.

There is a definite balance among the factors of furnace size, thickness of refractory, thermal conductivity of refractory, rate of power input and the number of hours used per day, which will give best results in the combined melting cost for power and for refractories. Further study of the problem may result in an even better balance of these factors.

The 250-pound furnace is a new size and full data on refractory life is not yet available, but the average will probably be well over 250 tons.

The 750-pound size, comparable in capacity to average sized furnaces of the induction type, is said never to have given a life of less than 375 tons, and the average is 500 to 600 tons. The one-ton size may give only 250 tons if the lining is abused in mechanical charging by dropping heavy ingots in from a considerable height without first placing a cushioning layer of borings. With care, however, the furnace should average 1000 tons, figures running from 600 to 2000. The lining life has steadily increased as users gain experience with the furnace, and as the makers are succeeding in impressing on the users the desirability of laying the brick tightly and without thick cement joints. Accurately fitting brick and close, tight joints are very essential. Given well-fitting brick, the life of the lining is probably more dependent on the conscientious work of the brick layer than on any other factor.

Aside from the damage by careless charging, the failure of a lining is primarily due to penetration of metal into the lining. Not only does this damage the lining by expansion of the penetrated metal in heating up after it has frozen during the night, but it increases the thermal conductivity of the lining. The penetration of zinc vapor into the part which is the roof during the first part of the heat, before rocking starts, is as serious or more so than the penetration of liquid metal. The aluminous refractories generally fail by slow disintegration in the "roof" and in the un-washed ends, the process seemingly involving a spalling off of very minute particles, probably due to the entrance of zinc vapor, subsequent condensation, freezing when the furnace cools and expanding enough to cause this spalling when it is again heated.

This results in a gradual thinning away of the "roof" portion and finally the collapse of the inner course of the lining at that point follows. The "initial hearth" portion is less damaged than the "initial roof" portion.

It is probable that after 1500 heats, in any size furnace, the extra power required by permeation of the lining by the metal rises to a point where it would be cheaper to tear out a lining that might last 500 more heats, as more than the cost of the lining might be paid to the power company for radiated energy in the balance of its life. The average energy consumption over a period of 1500 heats is about 5% higher than with a brand new lining. The above figures refer to Corundite linings.

Some users have adopted Lawtonite, a refractory stated to contain about 40% fire clay and balance carborundum, although other sources of information report the refractory contains zirconia and carbon also. The cost is more than double that of Corundite. One user who was averaging 700 tons of red brass melted on Corundite, got 2700 on a Lawtonite lining. Others say that the life is doubled, while still others can see no appreciable difference. Lawtonite does not appear to stand abuse in charging any better than Corundite. On account of the greater thermal conductivity of carborundum, a Lawtonite lining will presumably show a slightly higher power consumption.

One user of a one-ton Booth furnace, after poor results in a four-piece lining, installed in August, 1921 a lining of Carbofrax (clay-bonded, high carborundum content) brick backed up by Corundite and in turn by Sil-O-Cel. This lining has been used in 24-hour service on 60:40 brass, is still in service, and looks good for an indefinite further period, after melting about 4000 tons. Beside the long life the lining is liked because zinc oxide or dross does not cling to it, and there is no accumulation to be fluxed out at intervals. Although such a lining is expensive, the users say it has been a "wonderful investment." But they are careful to state that the lining has so much heat capacity and such high conductivity as to take a long time to heat up after the Sunday shut-down, and they believe that it would be quite as unsatisfactory in daylight service on the score of lower production and higher power consumption, as it is satisfactory on refractory life for 24-hour service.

The furnace uses an average of 290 kw.-hr. per ton on 60:40 brass in 24-hour service. The users do not consider this much higher than would be required with a Corundite lining. Since one-ton Detroit furnaces, Corundite lined, operating on 60:40 for only 16 hours a day have given long averages of 225 kw.-hr. per ton, it would appear that the remarkable refractory life is obtained at some sacrifice of efficiency and other users might conclude that the Carbofrax lining increased the over-all melting cost despite its long life.

The experiences with Lawtonite and Carbofrax bring up again the question of a graded brick, approaching Carbofrax in composition on the working face and approaching Corundite on the other, with the carborundum content decreasing uniformly from one side to the other. Some experimental work has been done on the production of these graded refractories.

The refractory problems of the moving indirect arc type furnace seem to be in fair shape. The furnace does not ordinarily go out of commission suddenly through refractory failure as is the case in the failure of the resistor trough of the Baily, and metal seepage into the lining has no effect on the electrical operation of the furnace, as it does in the induction furnace. The furnace can be turned so that any part of the circumference of the lining can be patched with the spot to be patched at the bottom, so that the patch is held in place by gravity while being sintered in. The moving indirect arc type shows fully as good a life in melting red brass as it does on yellow, some users say rather better, and even highly leaded red brass has no marked destructive effect.

Progress on this type will be made with a better balancing of furnace design with the properties of the refractories, in prevention of penetration of the refractories by metal, and by insisting on brick that can be fitted accurately and on fitting them accurately. The suitability of three-piece linings for the smaller sizes is still an open question.

Induction

The Ajax induction furnace (Figs. 6 and 7)[1] has had several hundred furnace-years' use on yellow brass, and the refractory problems on alloys high in zinc and low in copper (not over 75% Cu) are pretty well whipped. The resistor or secondary loop of the furnace, as shown in Fig. 8, is of peculiar shape, and this part is usually rammed up about a wooden form which is then withdrawn and a resistor ribbon slipped in and clamped together to form a solid secondary loop. Sometimes a brass form is used and left in place and current passed through it to dry the lining and later to melt the form, but this tends to crack the refractory due to expansion. Sometimes a form of paraffin in which a resistor is embedded is used, or a hollow sheet form of copper or brass used, either method avoiding expansion stresses. Some users air-dry the rammed-up shell and then heat it slowly in an oven before assembling the furnace and preheating it with a solid resistor within the loop. Others start heating by the resistor without air-drying, and have been able to start melting with the relined furnace 36 hours after the furnace was shut down, while the slower method takes a week or more.

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[1] *Loc. cit.*, **6** [4], 605, 606(1923).

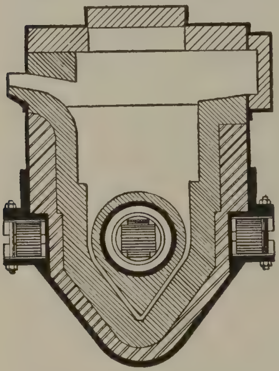
Fig. 8.—Section of Ajax-Wyatt furnace.

The refractory used for these rammed-in linings is an asbestos fire-clay mixture such as Johns-Manville asbestos cement No. 26 or 29, usually No. 26, or a similar mixture put out by the furnace makers. This seems to have the necessary properties of low thermal conductivity, some flexibility and ability to resist cracking due to the asbestos, and sufficient refractoriness for handling alloys with under 75% copper.

The usual rolling mill mixtures, containing under 3% lead, work all right with this lining, but alloys high in lead tend to give penetration.

The lining may fail either in infancy or in old age. Early failure is generally due to cracks, present before the first heat is made, or incipient and opening up soon. Since this type of furnace either melts 24 hours a day or has power kept on at night to keep the metal in the resistor loop melted, seldom or never being emptied and allowed to cool, there is a minimum of sudden temperature changes, and unless a crack is formed from steam pressure in drying out (the lining is mixed with the minimum of water for ramming) it should not crack thereafter.

The asbestos shreds tend to bridge an incipient crack and prevent molten metal from entering. If cracks do develop and metal works through them to the shell, so that a short circuit can occur the electrical conditions are disturbed and the furnace will no longer operate. In the early days a good many linings never completed the first heat, but with experience in ramming and drying out, early failure, though not absent, is more rare, and the rammed-up linings, in 60-kw. furnaces of 675 lbs. pouring capacity average at least 500 and probably 600 tons, and occasional lives of 3000 tons have been attained. One user gives the cost of lining, installed, as $90.

When the yellow-brass furnace linings die of old age, their failure is generally due to building up of incrustations of zinc oxide or dross in the resistor tube to such an extent that it can no longer be scraped out with high speed steel or nichrome tools used for this purpose, and chokes the channel so that the secondary is no longer of the proper size. Sometimes such cases can be helped by shifting to an alloy high in copper which has more scouring action on the tube and may clean it out.

Some users mix old crushed fire brick with the asbestos cement mixture for linings for yellow brass, but opinion is divided as to whether this is an improvement or otherwise.

Preformed linings of the shape shown in Fig. 9 have been tried out for several years in the Ajax furnace. Outside of one firm, no one seems to be using them now for either yellow or red brass. The superintendent of mechanical equipment of this one firm recently told the maker of the furnace that the preformed lining had been adopted at one of the plants and would be at all plants when the furnace shells were modified to allow it. A recent letter from the technical superintendent of the same firm to the writers states, however, that none but rammed linings are in use and that while the preformed linings had been tried out, all shops had gone back to the rammed linings.

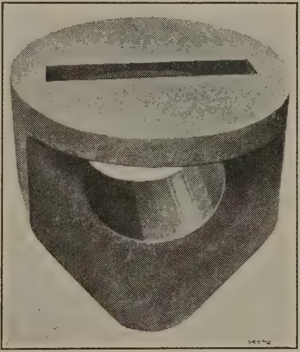

Fig. 9.—Preformed lining (resistor loop section) of Ajax Wyatt furnace.

The rammed asbestos cement (plus fire clay or ground fire brick) lining appears highly satisfactory for yellow brass. The temperatures required on the high zinc brasses are seldom over 1125°C or 2050°F and in the induction furnace the lining is not hotter than the metal.

The higher temperatures required for "nickel silver" or nickel brass and for red brass, sometimes going up to 1350°C or 2450°F play havoc with the asbestos-clay linings, for even though such linings may show a higher cone-test, in continued service they soften and allow metal to permeate them. Asbestos of course does not retain its flexibility but gets brittle at such temperatures, though it may still be a suitable bond. But for red brass the bulk of the mixture must be more refractory than for yellow and the lining must resist penetration by alloys that are more fluid than yellow brass is.

While the red brass (90 Cu, 10 Zn) of the rolling mill does not offer insurmountable difficulties, the red brass (85 Cu, 5 Zn, 5 Sn, 5 Pb) of the sand casting foundry and the other leaded alloys that must be handled, present worse difficulties.

Much work has been done on Ajax furnace linings for red brass in the effort to extend the field of the furnace beyond its proven one of yellow brass. The materials which best resist the action of the red metal seem to be fire-clay graphite (which involves rather too great heat loss), Thermolith (a chromite composition), Arcofrax (a high Al_2O_3 clay of the Corundite class) and Diamel (MgO Al_2O_3). A French type of three-phase induction furnace is said to use a fused sillimanite-alumina mixture with success. Magnesite has been tried in induction furnaces for red brass and found unsatisfactory. One rolling mill finds Thermolith the most satisfactory. A foundry running leaded red brass very hot with 8-hour melting with power on all night, has, besides many poorer results, obtained between 125 and 230 tons with an over-all average of perhaps 100 tons. The power consumption is 375 to 400 kw.-hr. per ton. Another plant, on 90 Cu, 10 Zn, could not get over 15 tons on an unstated lining, but with a refractory called Durastix, of composition unknown to the writers, got up to around 60 tons. Still another, on 90:10 with a rammed lining of composition also unknown, costing $150 installed, averages 125 tons. On nickel-silver this lining has given this plant a maximum of 100 tons.

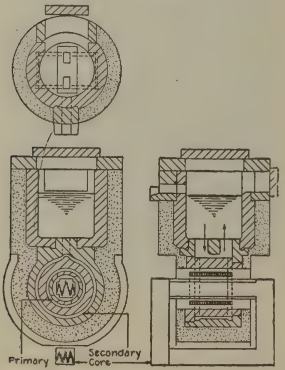

FIG. 10.—General Electric induction furnace. Sectional view showing the IFS-75 kw. repulsion induction furnace.

As the furnace maker states the problem, it is necessary to find a lining which will average upwards of 100 tons on red brass and give uniform life.

Users state that the failure of an Ajax lining on 90:10 occurs because of the lining becoming permeated with metal so that the lining about the resistor tube becomes conducting, the furnace takes too much power, beyond the transformer capacity, and the power factor drops way down. The thermal efficiency drops also so that while a new Ajax lining in 24-hour operation melts 90 : 10 at 285 kw.-hr. per ton the average is about 335 kw.-hr. per ton.

Though the users appear to consider a preformed lining as more convenient to install, the maker of the Ajax furnace appears more optimistic over the chances for a preformed lining for red brass than the users do. Since several materials withstand the action of red brass fairly well, the maker considers that the troubles are purely mechanical, connected solely with the design of the block and that these troubles will be eliminated by the cut and try process during a long series of tests already planned to be carried out with the coöperation of half a dozen users. The makers report that a lining embodying a new principle for which patent application has been made, has now been in use for a considerable time. They believe that such lining gives promise of better performance than any lining heretofore used in the service of melting the high copper alloys known to the foundry trade as red brass.

General Electric Induction Furnace

The General Electric Co. recently put out an induction furnace of very similar design to the Ajax, but with a different form of resistor loop. (Fig. 10.) The General Electric uses preformed fire-clay blocks entirely, the shape being shown in Fig. 11.

These blocks are said by a user to cost $350 installed. One firm melting a yellow brass of 65 Cu, 33 Zn, 2 Pb on 9-hour operation finds the life to run from less than 85 tons, to about 350 tons with the average probably not better than the guarantee, which is put in days, but is equivalent to 85 tons in this case. The makers state that consistent results have not yet been attained, and ascribe it to uneven control of manufacturing conditions in making the refractories and therefore subject to correction, which is "expected to take place in the near future." Refractory manufacturers are in a better position than the writers to judge the chances of making good on such an expectation.

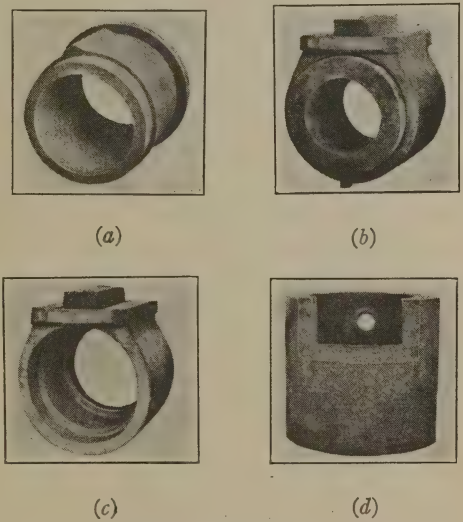
(a) (b) (c) (d)

FIG. 11.—Preformed lining of G. E. furnace.
(a)—Inner refractory shell of heating chamber
(b)—Lower or heating chamber assembled
(c)—Outer refractory shell of heating chamber
(d)—Upper or melting chamber

Another firm, melting 90 Cu, 10 Zn, 24-hour operation, has obtained as high as 300 and 350 tons though most runs were very much poorer. The average melting rate throughout the life of the lining, which gets soaked with metal, was 365 kw.-hr. per ton, with the old width of slot in the resistor tube, *i. e.*, the furnace was some 10% less efficient than the Ajax although it was of larger capacity and used higher power input. With the new, narrower slot the efficiency of a General Electric furnace with new lining is stated to be slightly above that of the Ajax with a new lining, as would be expected because of the higher power input.

In the same sizes and with equal power input the two designs of induction furnace are not expected to show any difference in efficiency, though the General Electric is said to give only 55 to 60% power against 60 to 65% for the Ajax on 90:10 brass.

It appears that while the induction furnace with a rammed lining can melt yellow brass in 24-hour operation at 225 kw.-hr. per ton and at about 15 cents per ton for refractory costs, on red brass the power consumption runs over 300 kw.-hr. in 24-hour operation and around 375 kw.-hr. for 8-hour operation, with lining costs running from 65 cents in the best case to $10.00 per ton in the worst and an average of perhaps $1.20.

With a preformed lining on 90 : 10, 24-hour operation, the refractory cost may be as low as $1.00 per ton or higher than $4.00, with the average perhaps around $2.50.

On yellow brass, where the induction furnace lining problem is in good shape, that fact, the good efficiency on 24-hour operation, and the avoidance of electrode costs, make the induction furnace hard to beat, and it is only natural that the rolling mills which have adopted it for yellow metal should wish to extend its use to nickel silver, red brass and bronze in order to have uniform furnace practice on all alloys. However, there is a decided tendency on the part of the rolling mills to utilize Detroit, Booth, Bennett. or other electric furnaces for the higher melting, higher copper alloy because of the refractory troubles of the induction type. Unless the refractory situation is cleaned up this tendency is likely to continue.

The entrance of the induction furnace into the jobbing foundry field where 8-hour operation on leaded red brass is the rule, is not progressing very rapidly and most of the plants which are trying it out state that they consider it to be still in an experimental status.

In fact, in the work being done with the Ajax furnace on red brass, the expense of the experimentation with refractories is being borne by the furnace maker instead of by the user.

In such service the induction type is generally less efficient than the moving indirect arc type and there is only a slight margin in favor of the induction furnace on its cost of power plus labor per ton against the cost of power plus electrodes plus labor per ton for the arc type. At present the margin against the induction furnace on refractory cost is so great as to more than wipe out the margin piled up by its other advantages.

As the writers see it, the induction furnace makers will be forced to improve the refractory life on red brass and similar alloys very materially or else accept the present situation as inevitable and withdraw from that field.

Summary

Summing up the situation, the old type Baily furnace has some refractory troubles, worst in the carborundum trough, which will be accentuated in the new design, but these troubles will have to be accepted or solved if the efficiency is to be improved enough to keep that furnace in the running.

The Booth and Detroit furnaces do not have serious refractory troubles but have opportunity for marked improvement in efficiency by engineering design calculated to make the most of the available properties of the refractories. Their most serious problem is in avoidance of penetration of the refractories by the metal, both as liquid and as vapor and in getting the bricks laid in proper fashion. The question of standard brick *vs.* large special shapes for the smaller sizes is not yet definitely settled.

The Ajax furnace has no serious problem in the refractory field for yellow brass. With the preformed lining, the General Electric furnace does have a problem there, and both furnaces, whether with preformed or rammed linings, have a problem of the first magnitude in the red brass field.

The question is, what can be done toward solving these problems? It would appear to the writers that since the question of metal penetration is very important something might be done by the application of electrically fused or otherwise fully preshrunk refractories, selection of refractories for low thermal expansion, and especially in the use of different sizes of grains so as to minimize voids and favor "close-packing" of the material.

Impregnation of the brick or of the rammed lining with hydrocarbons has been suggested, the idea being to fill the pores with the coke resulting from the decomposition of the hydrocarbon.

The problem has many sides. There is nothing gained by working out a refractory of infinite life if it is going to lose so much heat through the walls as to raise the energy requirements enough to pay for a cheap lining every few weeks. The cost factor is always present and the aim in the development of refractories must be to reduce the over-all cost of melting, and in this a multitude of factors have to be considered. No very prompt solution of the problem is to be expected, from its very nature. Most of these vitally interested are awake to the problem and are earnestly trying to solve it. The problem will work out in time, and the furnace user must draw on his stock of patience till he hits the solution, or till somebody else hits it and tells him about it.

The writers are inclined to think that the slow process of solution of the general problem would be accelerated if the furnace users would put on record either by detailed reports of the results of past experiments in the form of papers to some such SOCIETY as this; or, better, by submission of such reports to some committee which would sort and tabulate them. There have been enough experiments made to form a very useful foundation for future experiment, but data on them are available to very few people. Even the furnace makers, who have the most information, do not get all the data and they can gain from the experience of users of other furnaces and from the suggestions of refractory makers, if the refractory makers understand the problem in all its details.

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THE DEAD BURNING OF DOLOMITE.—IV[1]

By James Thomas Robson and James R. Withrow

Dolomite Bricks

Since member 2A14 gave all indications of being dead burned and contained but 10% of flux, it was decided to study the composition further as to its possibility for making regular size dolomite bricks, using 100-mesh dolomite throughout.

Hand molded briquettes about 5 x 2 x 2 inches were made of this composition. These were burned to cone 16 down. The bricks were set on chrome powder sprinkled over silica bricks, since no magnesite bricks were at hand.

It was found that a very slight dusting had taken place on the bottom, otherwise the bricks came out in very good shape. One of these bricks was tested in the hot water slaking test and remained there 20 days, after which time it broke into 4 pieces. The other bricks were placed outside in the air, where they have already remained for 15 continuous months without any alteration whatever.

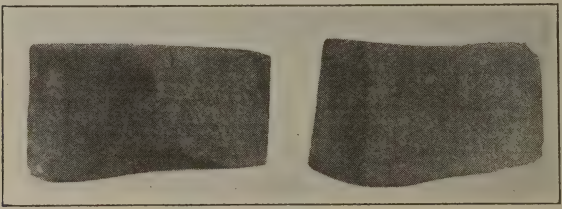

Fig. 32.—RA_{14} and R_1A_{14}.

Large sized bricks, $4^3/_8$ x $8^3/_4$ x 2 inches, of this composition were made by pressing the bricks out on a hydraulic press using 685 pounds per square inch pressure and 12% water for plasticity. These bricks were burned to cone 17 down and lost approximately 43.6% in weight on the dry weight basis. Both of these bricks cracked during burning. However, they were very firm and dense. They were burned on magnesite brick and no trace of dusting was noted where they came into contact with the magnesite brick.

One of these bricks was heated in an autoclave in water for 2 hours, during which time the gage pressure increased to 65 pounds per square inch. After this treatment the brick was unaffected. It was then again tested in the autoclave at 70 pounds per square inch gage pressure, for two hours at the end of which time it still remained unchanged. This brick RA14 has been standing in the laboratory for 15 months with no sign of alteration. The other brick R1A14 has been standing outside in the open air for the same length of time with no visible change having taken place. These two bricks are shown in Fig. 32.

Bricks from Calcined Dolomite

Brick XA14.—A batch of dolomite was calcined at cone 9. On treatment of this dolomite with hydrochloric acid, no traces of CO_2 were given off so that it was assumed that the dolomite was completely free from CO_2. According to the analysis of this dolomite, the CO_2 amounts to 46.8% by weight so that this amount was deducted from the batch weight which was made up as follows:

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[1] Published by permission of the Director, U. S. Bureau of Mines. See "The Dead Burning of Dolomite.—I," *Jour. Amer. Ceram. Soc.*, **7** [1], 61(1924); *ibid.*, II, **7** [2], 14; III, **7** [3], 207 (1924).

Dolomite calcined at cone 9	82.66%
Fe_2O_3	3.47
Al_2O_3	6.94
SiO_2	6.93
	100.00

Here it is seen that 82.66% of calcined dolomite with the above amounts of fluxes correspond to 90% of raw dolomite plus 10% of fluxes which is the composition of A14.

This batch was mixed with an excess of water and allowed to stand over night in order for the free lime to slake. It was then passed through an 8-mesh screen, sprinkled with H_2O and pressed into a brick about $8^3/_4$ x $4^3/_4$ x $1^9/_{16}$ inches in dimension, using 645 pounds pressure per square in. The water of plasticity on dry basis was 23%. This brick cracked considerably on drying.

Composition A14Y.—Determination of the true specific gravity of the raw dolomite by the pycnometer method gave 3.47. A batch of dolomite calcined to cone 5 gave a specific gravity of 3.08 by the pycnometer method, using kerosene as the immersion liquid. According to this specific gravity determination, 90 grams of raw dolomite correspond to 79.89 grams of this dolomite calcined at cone 5. A sample of this dolomite calcined at cone 5 gave no trace of CO_2 when treated with HCl and at cone 5 the dolomite should be completely free from CO_2 which would give a true specific gravity of 1.85. However, since the determinations for specific gravity checked at 3.08, it was decided to make up several batches assuming that only 11.2% loss in weight, as shown by the specific gravity, had occurred.

The following batch composition was made:

C. P. Fe_2O_3	2.23%
C. P. Al_2O_3	4.46
C. P. SiO_2	4.44
Dolomite calcined at cone 5	88.87
	100.00%

This composition is designated as A14Y.

Brick X1A14.—A brick was made of composition A14Y, again using 23% of water as in XA14. This water was added to the mix which was then allowed to stand for about one-half hour and then pressed into a brick $8^3/_8$ x $4^3/_8$ x $1^{13}/_{16}$ inches at 635 pounds pressure per square inch.

Brick X2A14.—This brick was made up of A14Y composition. About 34% of water was added and the mix allowed to stand in a humidor for about 20 hours. It was then screened through an 8-mesh screen and pressed at 370 pounds per square inch pressure into a brick $8^3/_4$ x $4^3/_8$ x $2^1/_8$ inches. This brick required only 200 pounds per square inch for forming because of the fact that it contained such a high per cent of water.

Small white particles of lime were noticeable throughout this brick.

Bricks X3A14, X4A14 and X7A14.—Made of composition A14Y except iron oxide analyzing 97.8% Fe_2O_3 was used in place of the 99.99% Fe_2O_3. This Fe_2O_3 was calculated to 100% Fe_2O_3 and the corrected amount used. Also, commercial Al_2O_3 and SiO_2 were used which in both cases analyzed over 99% pure. These bricks were pressed at 550 pounds per square inch.

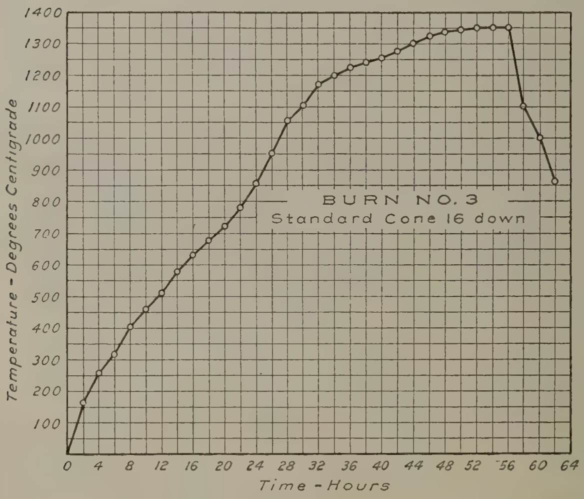

FIG. 33.

Bricks X5A14, X6A14, X8A14, X9A14, X10A14, X11A14 and X12A14.—These bricks were made of composition A14Y using 645 pounds per square inch pressure. They were mixed with different percentages of water as shown in Table IX, and pressed into bricks.

Raw Dolomite Bricks

Brick R2A14.—This brick was made of raw dolomite of the same composition as A14 using the C. P. oxides as fluxes. It required 12% of water for plasticity and 610 pounds per square inch pressure before it could safely be removed from the press mold without breaking. With 12% water of plasticity, it was found impossible to obtain a solid brick capable of handling with less than 610 pounds per square inch pressure.

Bricks R3A14 and R4A14.—Made of raw dolomite and used the 97.8% Fe_2O_3 and commercial Al_2O_3 and SiO_2, calculating all to the composition of A14. These bricks were treated with 12% of water, allowed to stand over night in a humidor and pressed into brick at 665 pounds per square inch.

The data regarding all these bricks are given in Table IX. They were burned to cone 16 down according to Fig. 33.

TABLE IX

Body	Pressure applied to mold. Lbs. per sq. in.	Per cent water of plasticity, dry wt. basis	Per cent volume drying shrinkage (plastic basis)	Condition after drying	Burning loss (dry wt. basis), per cent	Per cent volume burning shrinkage (dry basis)	Condition after burning to cone 16	Thickness of dry brick in inches
R2A14	610	12	4.6	O. K.	47.0	63.8	Cracked	$2^{7}/_{16}$
R3A14	665	12	8.6	O. K.	47.7	65.6	Very good	$1^{23}/_{32}$
R4A14	665	12	4.6	O. K.	47.2	65.1	Broken in middle	$1\,^{7}/_{16}$
XA14	645	23	...	Badly cracked	....	....	Badly cracked	$1\,^{9}/_{16}$
X1A14	635	23	2.7[1]	O. K.	....	....	"	$1^{27}/_{32}$
X2A14	370	34	6.5	"	....	64.6	"	$2\,^{5}/_{64}$
X3A14	550	40	2.9	"	26.7	67.2	"	$2\,^{1}/_{64}$
X4A14	550	40	0.9	"	24.2	68.4	"	$1^{23}/_{32}$
X5A14	645	40	2.3	"	26.2	72.5	"	$1^{21}/_{32}$
X6A14	645	40	2.5	"	26.9	72.0	"	$2\,^{1}/_{16}$
X7A14	550	60	5.3	"	27.7	....	"	$1^{11}/_{16}$
X8A14	645	21	11.3[1]	"	26.8	70.0	"	$1^{15}/_{16}$
X9A14	645	40	2.9	"	29.5	73.7	"	$1^{23}/_{32}$
X10A14	645	45	5.1	"	28.7	70.4	"	$1\,^{7}/_{8}$
X11A14	645	45	7.8	"	....	....	"	$1^{13}/_{16}$
X12A14	645	45	...	"	27.9	....	"	$2\,^{1}/_{16}$

[1] Expansion.

The drying volume shrinkage and burning shrinkage were determined by calculating the volume of the bricks from the measurement of their thickness, width and length, both before and after drying and burning.

Results of Burn 3.—Brick R2A14 was cracked through into three pieces and had several horizontal cracks along the bottom side on which it was standing when burned. After standing for about 10 weeks, the bottom along these cracks broke into several small pieces. This brick was no doubt too thick to burn without cracking.

Brick R3A14 was in very good shape. It is a very dense and solid heavy brick, which after 15 months has shown no sign whatever of cracking or slaking in any way. Fig. 34 shows this brick; also R4A14.

Brick R4A14 was broken down through the middle. Otherwise, it resembled brick R3A14 very closely, which was of the same composition. After 15 months' standing in the laboratory, no visible change has taken place in this brick.

All bricks with prefix X on the designation mark, where previously calcined dolomite was used in making the batch, were badly cracked after burning, and had many spots of dicalcium silicate throughout. After standing for about 28 days, all of these bricks slaked and disintegrated. Several of them, after standing in the laboratory and slaking for about eight months, are shown in Fig. 35.

The amount of pressure varied from 370 pounds to 645 pounds per square inch in making bricks with the calcined dolomite mixture, but since all of these bricks were badly cracked, the pressure applied evidently was of no help in preventing this cracking.

Table IX shows that, using raw dolomite, the necessary amount of water required to form bricks sufficiently strong to remove them from the mold without cracking or breaking is 12% of the dry weight of the mixture.

The loss in weight when burning the raw material was about 47%. The theoretical loss due to evolution of CO_2 when 90% of dolomite is present is 43%. This leaves 4% loss in weight, about 2% of which is probably due to the dehydration of the Al_2O_3 which combines with considerable water probably forming in some cases $Al_2O_3.3H_2O$. This water of hydration is not lost until a temperature of 300°C is attainable. The other 2% is probably chiefly due to volatilization at the burning temperature cone 16.

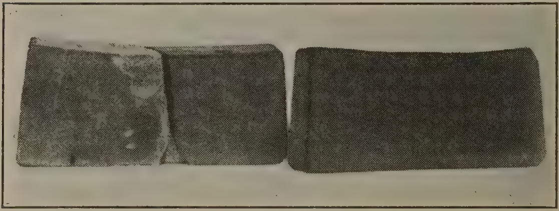

Fig. 34.—R_4A_{14} and R_3A_{14}.

The burning volume shrinkage is about 65%, which is so excessive that it is practically impossible to make a brick of the raw material on a commercial basis without cracking. As noted, however, brick R3A14 is an exception.

Brick R2A14, which was $2^7/_{16}$ inches thick when dry, cracked very badly whereas R3A14 and R4A14, which were only $1^{23}/_{32}$ and $1^7/_{16}$ inches thick, respectively, showed a much greater improvement over the thicker brick R3A14, being perfectly solid, and R4A14 being cracked down through the middle. (See Fig. 34.)

Brick XA14 made of dolomite, calcined at cone 9, cracked badly on drying and hence was badly cracked after burning. This brick showed considerable dusting throughout, due to the dicalcium silicate, and after about three weeks it started to disintegrate. After 10 months' exposure in the laboratory, most of this brick had disintegrated.

The increased amount of water required for forming the calcined dolomite mixtures above that required for the raw dolomite mixtures is due to the slaking or chemical combination of water with the free CaO and perhaps MgO in the calcined dolomite.

The loss in weight after burning averages about 27% in the case of the brick made from the calcined material. The theoretical loss due to driving off the chemically combined water from the double salt $Ca(OH)_2$-$Mg(OH)_2$ is 27.2%. Assuming this double salt to be 90% pure, as is the case with these bricks containing 10% of flux, the loss in weight should be 90% of 27.2=24.5%. The cause of the loss in weight of these bricks is thus chiefly due to the loss of chemically combined water and to a slight extent due to the fact that some of the water which combined with CaO was replaced by CO_2 while standing in the air before burning. This accounts for the fact that the loss in weight was 27% instead of 24%, as would be the case if no CO_2 were taken up by the lime.

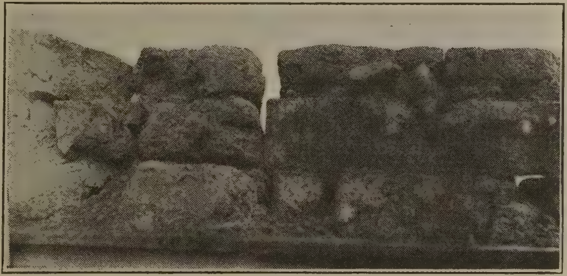

FIG. 35.—Air slaked dolomite bricks.

Bricks X1A14 and X8A14 were made using only 23% and 21% of water for plasticity, respectively. On drying, these bricks expanded rather than contracted. The water content of these bricks was below 24.5%, which as explained above is the amount required for complete hydration of the CaO and MgO; hence all the water used no doubt went into combination, on standing, of the bricks, leaving no shrinkage water present. Hydration of lime causes expansion.[1] Where more than 24.5% of water was used, the excess shrinkage water present caused a much greater contraction than the expansion caused by the hydration of the CaO and MgO; hence the bricks contracted during drying.

The average amount of water of plasticity used for making these bricks of previously calcined dolomite was about 40%. In brick X7A14, 60% of water was used. This brick was so badly cracked after burning that its contraction could not be determined. This was also true with bricks XA14, X1A14, X1A14 and X12A14.

The effect of making these bricks under different pressures cannot be drawn from this study since all the bricks of XnA14 composition cracked after burning.

Bricks XA14, X1A14, X2A14 and X11A14 had pieces broken from them in the kiln and could not be weighed after burning.

In general, it is thus seen that bricks made from the dolomite calcined alone and then adding a flux is impractical due to hydration of the free CaO and MgO.

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[1] A. C. Davis, "Portland Cement," p. 201.

Bricks made of composition A14 using raw dolomite will no doubt be successful if some means can be found for overcoming the cracking which is due to the high shrinkage.

Burn 4.—Calcined Plus Raw Material

Several bricks and briquettes of composition A14 which had been exposed to the outside and inside slaking tests were ground to pass a 20-mesh screen.

This crushed calcined dolomite was mixed in a dry pan for two hours with raw composition A14 (100-mesh) in the proportions of 80% of calcined A14 and 20% of raw A14. Also a batch was made using 60% of calcined A14 and 40% of raw A14 composition. These were designated as R20CA14 and R40CA14, respectively.

These compositions were mixed with water and allowed to stand over night. After standing, they became very hard, showing that the calcined material A14 possesses hydraulic properties. These hard batches were then broken and rescreened through an 8-mesh screen. About 20% of water was added and the material pressed into bricks, using 1,000 pounds and 3,000 pounds per square inch pressure. After drying at room temperature for two days, the outside surface cracked badly in all cases. These cracks did not penetrate through the center of the bricks, but only about $^1/_4$-inch deep through the outside surface, which was hard and shell-like due to the fact that it was pressed denser than the inside which was soft and punky. These bricks were again crushed and screened to make the following bricks:

Brick R40C1A14.—One half of R40CA14 was treated with 22% of water, rescreened through an 8-mesh screen, allowed to stand 24 hours in a closed vessel and then pressed into a brick using 480 pounds per square inch. This brick was labeled R40C1A14. Although this brick dried without cracking, it was so fragile that when being lifted to place in the kiln, it cracked very badly throughout.

Brick R40C2A14.—This brick was made from the other half of batch R40CA14, using 12% by weight of thin coal tar and pressing at 480 pounds per square inch pressure. This brick, however, broke on handling after several hours' standing. It was then disintegrated by hand and after heating for about one hour over a Meker burner, it was treated with 12% of hot tar which when cold was much thicker than the previous tar used. (See analysis, p. 307). However, 12% of this heavy tar proved to be too much, since when pressed to 480 pounds per square inch pressure very little visible compression of the brick took place, due to the large amount of thick tar and when removed from the die, the brick was of rubber-like consistency. This brick dried without cracking and could be roughly handled without harm.

Brick R20C1A14.—This brick was made of composition R20CA14 using 12% of the heavy tar analysis which is given below, and using 480 pounds per square inch pressure. This brick formed very well when pressed with the hot tar and dried without cracking, being very firm and solid, so that it could be easily handled.

Brick R20C2A14.—Composition R20CA14 was thoroughly mixed by hand with 7% by weight of powdered caustic magnesite made from Grecian magnesite calcined at 1000°C. The batch taken required 30% of water before it could be successfully molded. Although this brick dried fairly well without cracking, it was so fragile that when being set in the kiln, it cracked throughout.

TAR ANALYSIS

	Per cent		Per cent
Bitumen	77.88	Specific gravity at 25°C.	1.237
Insoluble organic matter	22.05	Float test at 50°C.	2.56
Ash	0.07		
	100.00		

Bricks X13A14 and X14A14.—As was mentioned in the description of the preparation of composition A14Y, it was thought that perhaps the dolomite calcined at cone 5 had been completely freed from CO_2, although the specific gravity determinations seemed to indicate otherwise. Since bricks made of composition A14Y, assuming that the dolomite was not completely decomposed, had all slaked down, a batch of the percentage composition A14 was made assuming that all the dolomite calcined at cone 5 was completely free from CO_2. This percentage composition corresponds to that of XA14 previously mentioned. It was molded into brick X13A14 using 550 pounds per square inch pressure and brick X14A14 which was molded by hand after a sufficient amount of water had been added to make it soggy-like. The amount of water in each case was not measured. Brick X14A14 dried without cracking, while brick X13A14 dried fairly well, but had two small cracks in the center. However, no further cracking occurred with rather rough handling of the bricks.

Calcined Material

Compositions A14, D6 and D9.—Batches of composition corresponding to A14, D6 and D9, all of which stood up against slaking in the air and water, were made. These were calcined to remove all of the shrinkage and then made into large size brick.

The A14 and D6 batches were made by tempering with water into small balls about $1^1/_2$ inches in diameter. Batch D9 was made into small circular plaques about $2^1/_2$ inches in diameter and $^1/_2$-inch thick. This was done to determine whether or not the thinner plaques could be more thoroughly calcined than the balls. These were dried and calcined to cone 17 in Burn 2.

The compositions on dry basis of these batches in which C. P. fluxes were used are as follows:

A14		D6		D9	
Raw dolomite	90.00	Raw dolomite	85.00	Raw dolomite	85.00
Fe_2O_3	2.00	Fe_2O_3	9.00	Fe_2O_3	6.00
SiO_2	4.00	SiO_2	6.00	Al_2O_3	3.00
Al_2O_3	4.00	Al_2O_3	0.00	SiO_2	6.00
	100.00		100.00		100.00

Composition A14C.—A batch of A14 composition, using commercial materials for fluxes, was also calcined. In this batch North Carolina kaolin of analysis given below was used as the source of SiO_2, some Al_2O_3 and a slight amount of Fe_2O_3. For the deficient Al_2O_3, commerical Al_2O_3 analyzing over 99% pure was used. For the iron, Fe_2O_3 analyzing 97.8% Fe_2O_3 was used. The batch weight follows:

Raw dolomite	88.65
Fe_2O_3	1.92
N. C. kaolin	8.76
Al_2O_3	0.67
	100.00

This batch was mixed with water and molded by hand into a briquette about $1^1/_2$ x 3 x 5 inches and also into smaller briquettes about 1 x 1 x 3 inches. These briquettes dried without cracking.

ANALYSIS OF NORTH CAROLINA KAOLIN

Ign. loss	16.54
SiO_2	45.17
Al_2O_3	37.35
Fe_2O_3	0.60
TiO_2	0.03
CaO	trace
MgO	trace
K_2O	0.70
	100.39

Composition D9C.—This batch was made of the same materials as used in composition A14C, except that all of the Al_2O_3 was added in the form of North Carolina kaolin and the deficient SiO_2 was added as commercial flint.

The batch recipe follows:

Raw dolomite	83.85
Fe_2O_3	5.87
N. C. kaolin	7.95
SiO_2	2.33
	100.00

The batch was mixed with water and two briquettes $1^{1}/_{2}$ x 3 x 5 inches were molded by hand. These dried very well without cracking.

Results of Burn 4

The burning chart for this burn is given in Fig. 36. In this burn cone 17 was down in the front of the kiln and cone 17 was in the 3 o'clock position in the back of the kiln.

Brick R40C1A14.—This brick came out of the kiln badly cracked and bloated. It had a dull-like appearance. The shrinkage was not excessive. (See Fig. 37.)

Brick R40C2A14.—This brick was distorted and badly cracked longitudinally through the center parallel to the face of the brick and also vertically down through the center. The cracking in this case appears to be due more to the method of pressing rather than due to shrinkage which was not excessive. One face of the brick was perfectly smooth and intact so that probably the burning out of the tar binder did not cause all of the cracking, although the vertical disruption appears to be due to this. (See Fig. 37.)

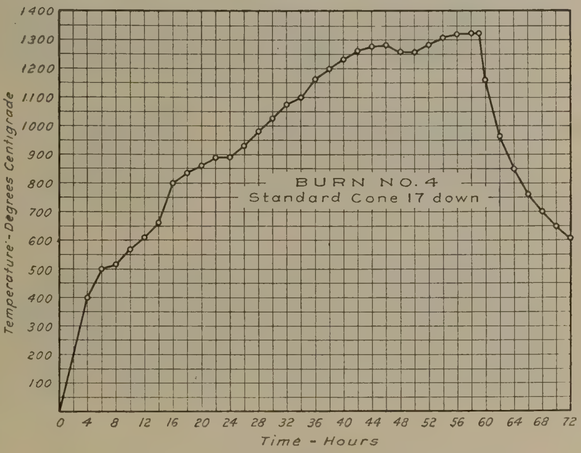

Fig. 36.

Brick R201CA14.—This brick was very badly cracked, broken in two, and bloated. This appears to be due to both the method of pressing and the tar used as a binder. (See Fig. 37.)

Brick R20C2A14.—This brick, made using caustic magnesia as a binder, had many cracks, mostly just on the surface. These cracks were formed while the bricks were being set in the kiln, the caustic magnesia not hardening sufficiently to make a tight bond. (See Fig. 37.)

Brick X13A14.—This brick had a few cracks which were formed while drying, but evidently did not have any cracks due to burning. This brick was warped. It was very dense, solid and almost glassy appearing. More bricks of this composition were made in the next burn in order to further study its adaptability as a refractory. No dicalcium silicate formed on this brick after standing in the air for 75 days. (See Fig. 37.)

Brick X14A14.—This brick had a surface similar to X13A14, but was badly cracked and disrupted. No dicalcium silicate formed on this brick upon standing for 75 days.

These bricks show that it is possible to dead burn previously calcined dolomite if sufficient flux is present. (See Fig. 37.)

Calcined Material.—All of these compositions calcined very well except the large briquettes of D9C, about one-half of which dusted down in the kiln. The large briquettes of A14C, however, where the commercial materials were used, proved to be very satisfactory, no sign of dusting or cracking occurring. (See Fig. 37.)

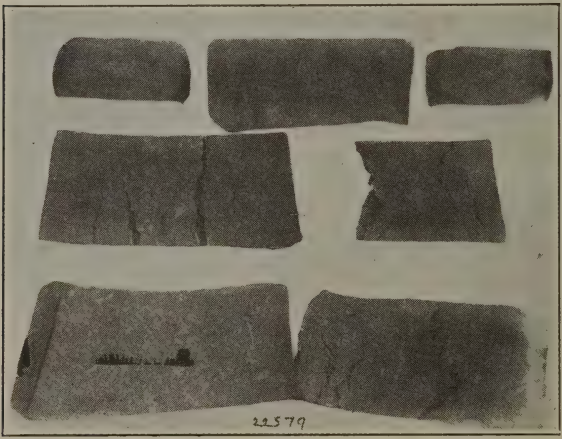

Fig. 37.—Top row, left to right, $A_{14}C_1X_{13}A_{14}X_{14}A_{14}$
Middle " " " " $R_{20}C_2A_{14},R_{20}C_1A_{14}$
Bottom " " " " $R_{40}C_2A_{14},R_{40}C_1A_{14}$

General Conclusions of Burn 14

The use of tar as a bond appears to be of no value, especially when part of the dolomite mixture has been previously calcined. In preparing dolomite-tar mixtures for basic converter linings, Backheuer[1] found that sintered dolomite cannot be used since it prevents absorption of the tar.

The use of water alone in forming bricks of the calcined plus raw material appears to be impossible because of insufficient bonding strength.

Caustic magnesia made from the Grecian variety does not exercise much bonding effect on calcined A14 composition.

Whether or not it is advisable to use a mixture of raw dolomite composition plus calcined dolomite composition cannot be decided from this brief study, although this method of using previously calcined A14 composition, of course, did decrease much of the shrinkage during burning.

---

[1] "The Preparation of the Dolomite-tar Mixture in Thomas (basic converter) Steel Works," *Stahl u. Eisen,* **41,** 954 (1921).

Further work done to determine the feasibility of using the calcined dolomite such as composition X13A14 as a suitable material shows it to be impractical. (See Burn 5.)[1]

In using calcined dolomite and then adding the fluxes, a brick molded under high pressure appears to be better than a hand-molded brick.

All of the compositions A14, D6 and D9 will calcine without dusting.

In composition A14 it appears to be possible to use North Carolina kaolin as one of the fluxes in place of free flint and some of the alumina. This kaolin is, of course, much cheaper than the pure oxides for which it is substituted.

Kaolin when used as a flux in composition D9 appears to cause excessive dusting and hence cannot be used.

All calcined bodies seemed to be burned completely through to about the same degree of vitrification so that the shape or thickness used within the limits herein is immaterial for calcining.

To be continued)

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[1] Description of Burn 5 will be given in *Jour. Amer. Ceram. Soc.*, May, 1924.

Official Personnel of Divisions—1924-25

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ORIGINAL PAPERS

THE USE OF BORIC OXIDE IN GLASS-MAKING

By W. E. S. Turner[1]

ABSTRACT

Boric oxide behaves differently from other glass-making constituents in that the variation of physical properties is not progressively continuous with a variation in composition. With increase of boric oxide content in sodium borosilicate glasses, the refractive index (μ_D) rises to a maximum as also does the annealing temperature, while the coefficient of thermal expansion reaches a minimum and then rises. The durability, or resistance to water and hydrochloric acid reaches a maximum when the glass contains about 12% of boric oxide and subsequently falls off very rapidly. There is, accordingly, a limit to the usefulness of boric oxide in glass.

Introduction

The advantages attending the use of boric oxide in glass-making, whether as borax or boric acid, are widely known although less widely understood. It is not only in the manufacture of optical glasses, scientific, illuminating and heat resisting glassware that its importance has been recognized but it has also had its application in the preparation of bottle glass and of glass for tableware.

Advantages in General.—The functions which recommend boric oxide in these different classes of glassware are several. In optical glasses specific influences on the value of the refractive index and dispersion due to the oxide are made use of, while increase in durability is also gained.

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[1] Recd. Feb. 12, 1924.

For scientific, illuminating and heat-resisting glasses the two most important properties which boric oxide bestows are an enhanced durability and a diminished coefficient of thermal expansion. A reduction in the viscosity of the molten glass is not the least important of the effects of this oxide, an effect of much value in glass-making practice.

This fluxing effect is the main reason for the employment of boric oxide or borax in the production of sealing-in glasses, for enamels, and generally as a medium for the application of pigments to glass. For the same reason, no doubt, it has found frequent use in some of the smaller glasshouses in England in which glass is melted from cullet, to which, in some cases, a small quantity of an alkaline salt, borax in particular, is added.

The object of using it in the production of colorless glass in tank furnaces does not appear yet to have been satisfactorily explained. We have found no evidence of any favorable influence excited by it in the decolorizing process. We have found, however, from our own experiments in this Department, that even small amounts, less than 1% in the glass, may quite distinctly influence the viscosity of the molten glass while a definite enhancement of the durability simultaneously occurs. That this last statement is a fact is proved in the case of potash- and potash-soda-lead oxide glasses by the experiments of Hodkin and Turner.[1]

Effect of Boric Oxide not Continuously Additive

The question as to whether or not boric oxide continues to exercise its valuable functions in a glass in direct proportion to the amount present has been obscured in the past partly by general experience and partly by the deductions associated with the various additive rules deduced by Schott, Winkelmann and others. It certainly is the general experience that a continued increase in the proportion of silica in a glass produces a continuously increasing viscosity, a diminishing thermal expansion and an enhanced resistance to corrosion; and the same continuity of change in physical properties with variation of composition also appears to be true of many other well-known constituents of glass.

It was pointed out however, by Zschimmer[2] in 1905, that when boric oxide was added to potassium silicate in continuously increasing proportions, the refractive index (μ_D) rose to a maximum value and then diminished. Recently it has been proved that a similar reversal occurs in several properties. Thus, we have shown[3] that not only does this apply to the refractive index of sodium borosilicates, but also to the density, the thermal expansion, the annealing temperature and the durability. These reversal effects are of the utmost importance both technically and in industry; for it has been demonstrated that a reduction of thermal expansion or of liability to corrosion by increasing the percentage of boric oxide only holds good up to a certain point beyond which the thermal expansion rapidly becomes greater as also the extensiveness of corrosion by water and chemical agents. Any attempts, therefore, to improve heat-resisting glasses or chemical glassware by the introduction of ever-increasing percentages of boric oxide are doomed to failure; there is a limit beyond which deterioration, not improvement, occurs.

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[1] *Jour. Soc. Glass Tech.*, **4,** 121 (1920).

[2] *Zeitsch. Elektrochem.*, **11,** 629 (1905).

[3] English and Turner, *Jour. Soc. Glass Tech.*, **7,** 155 (1923).

Effect of Boric Oxide on Resistance to Weathering

So far as weathering and resistance to chemical agents are concerned, boric oxide as an enhancer of resistance is something of an anomaly. Dralle[1] points out that the durability of a glass may be judged, in a rough and ready way, by the relative solubilities in water of the constituent oxides. Boric oxide, however, provides an exception to the rule. It is readily soluble in water and yet when present in commercial glasses, it has been found to enhance, very greatly in many cases, their resistance to the attack of water and of chemical reagents. The explanation of this phenomenon has generally been sought in the assumption of the formation of a class of compounds known as borosilicates, or, alternatively, in the suggestion that boric oxide substitutes silica in the silicates, the increased durability being actually due to an increase of free silica. Both theories appear to the author to lack positive evidence to support them.

Indications of the unreliability of boric oxide as a never-failing source of resistance to weathering have not been wanting in the past but they have not been widely known. There is no doubt that many old enameled glasses have suffered through the use of borax as the fluxing medium whereas those in which lead silicate has been employed have withstood the ravages of time. Schaller states that boric oxide added to sodium silicate at first diminishes the attack by water but later increases it. Sullivan and Taylor, in their account of Pyrex Glass, stated that they found a limit to the usefulness of boric oxide as beyond a certain percentage the glass containing it rapidly fell away in durability.

So far as the general problem of durability is concerned an exhaustive experimental study of the behavior of a large number of commercial chemical glasses led the writer with J. D. Cauwood[2] to the conclusion that, "Boric oxide increases the resistance of glass towards water, although it is probable that beyond a certain value (about 12 molecules per 100 molecules of silica), this effect declines. Boric oxide weakens the resistance of a glass towards alkali and hydrochloric acid."

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[1] "Die Glasfabrikation," 1911, p. 85.

[2] *Jour. Soc. Glass Tech.*, **2**, 233 (1918).

Recently it has been found possible to test this conclusion in a more direct manner, and based on work carried out in this laboratory by Miss V. Dimbleby, evidence that it is substantially true has been forthcoming.

Two series of glasses containing the oxides, soda, boric oxide and silica have been examined, one series containing approximately 20 and the second 10% of sodium oxide as constant quantities, the two variables being the silica and the boric oxide. Tests of the durability were made on grains of glass of 20- to 30-mesh by a method which has previously been described in a paper from this laboratory, boiling water or hydrochloric acid of 20.24% strength being the reagents and the time of their action one hour. The results are set out in Tables I and II.

TABLE I

THE ACTION OF BOILING WATER ON GLASSES OF THE SERIES CONTAINING APPROXIMATELY 20% Na_2O

Percentage composition of glass			Percentage loss of weight in water	Percentage Na_2O (total alkali) liberated
SiO_2	Na_2O	B_2O_3		
79.81	19.26	...	2.34	2.11
74.22	19.76	4.46	0.48	0.16
71.56	18.76	8.28	0.27	0.06
68.33	18.95	11.37	0.42	0.04
64.72	19.95	14.45	0.37	0.07
61.28	18.93	18.84	0.59	0.14
50.04	20.36	28.83	8.70	2.25
35.22	23.71	39.99	39.83	11.56
32.23	23.08	43.70	52.67	14.74

TABLE II

THE ACTION OF BOILING WATER AND HYDROCHLORIC ACID ON GLASSES OF THE SERIES CONTAINING APPROXIMATELY 10% Na_2O

Percentage composition			Percentage loss in wt. in water	Percentage Na_2O liberated	Percentage loss in wt. in HCl
SiO_2	Na_2O	B_2O_3			
74.91	11.26	12.45	0.13	0.004	0.09
70.75	9.79	18.71	0.44	0.07	0.67
67.18	10.13	21.81	1.55	0.36	2.73
61.94	11.19	25.82	4.67	0.89	32.49
57.87	9.55	31.26	12.80	2.42	41.01
52.11	10.34	36.17	30.82	5.50	49.00

It will be noted from Table I, that a minimum corrosion value occurs (based on the alkali liberated) when the glass contains approximately 11–12% B_2O_3. In other words, the maximum durability is reached at this point. A very rapid decline in durability occurs between 18–28% of boric oxide.

The tests with hydrochloric acid are not yet complete but the results so far obtained are parallel to those with water, maximum corrosion being obtained at the same point in the composition as is the case with water.

In the second series, containing approximately 10% of Na_2O, the corrosion continuously increases from the first glass examined. That glass, however, already contains 12.45% of boric oxide. It appears to be more durable than any number of the series in Table I and it may well be that maximum durability occurs when the glass contains approximately 12%. The corroding action of hydrochloric acid is parallel to that of water.

We thus have direct evidence that boric oxide improves the durability of a glass only up to a certain point and there is strong probability that approximately 12% in the glass marks its most useful limit.

DEPARTMENT OF GLASS TECHNOLOGY
THE UNIVERSITY
SHEFFIELD, ENGLAND

THE DEVELOPMENT OF TRANSPARENT COLORED GLASS IN AMERICA FOR GOGGLE PURPOSES[1]

By Edwin L. Hettinger

Introduction

ABSTRACT

Prior to the World War all of the goggle glass was imported from abroad. Necessity made us develop it in this country. Today all of the colors used for goggles are made near Pittsburgh. Glass is blown into large balls which are cut into strips and then cut into circles. Average thickness of glass is 2 mm. Average diameter of balls, 36 inches. Shades are graded into light, medium and dark. Colors are amber, smoke, fieuzal, amethyst and blue.

Historical The commercial production of colored glasses forms an important branch of glassmaking, although most of the coloring agents have been in use many years. Some early colors were produced by the Chinese and the Egyptians with whom the honors are about even on the priority of glassmaking.

While some colored glass was made in the United States prior to 1914, practically none of it was fit for use in ophthalmic, eye protection or technical industries. Several such glasses were tried but found to be of little value commercially. The glass directories listed 48 companies manufacturing illuminating ware, but very few of them had men familiar with transparent colors. The large users of these glasses urged the production of colored glasses that would not be prohibitive in price.

To the average individual the production of colored glass has not seemed to be a problem; even scientific men did not give it special attention. Thorpe, Knapp, Linton and Benroth did not include it in their classification.

Classification The first division would consist of pot colored glasses and stained glasses. While stained glass and glass enamel process have been wonderfully developed and improved, they still deserve a great deal of consideration.

Pot colored glass will be divided into the following: Transparent, Translucent, Opalescent, Luminous, Iridescent and Opaque.

Transparent colors are used for ophthalmic lenses, eye protectors, railroad signals, motor cars, light houses, ray filters, color processes, church windows and many other commercial and technical uses. Translucent glasses were easier to produce. The more colors the glassmaker produced the more could the decorator vary his shades and colors.

Luminous and "one way" glass was of some value, but limited in its uses. This was produced in small quantities.

Producers of illuminating glass have made wonderful progress in iridescent ware. The number of tints and shades have been increased in endless variety of color. These manufacturers also produce the opaque.

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[1] Presented at the Atlantic City Meeting, Feb., 1924 (Glass Division).

Industrial Developments since August, 1914

To find glass manufacturers producing transparent colors willing to develop transparent colored glass of uniform shade and density was a problem. Very few employed a ceramic chemist. Firms which had extensive laboratories did not have the shop organization to balance.

By the fall of 1914 the United States market was very short of these glasses. During the early part of March, 1915, fairly good transparent colors were being produced, but within a few months this glass showed signs of decay or weathering. The glassmaker knew it better as "sweaty glass."

The difficulty was in using a batch which would melt at too low a temperature. This low temperature was employed in order to save the pots. The batch did not produce a staple glass free from lines and striae. With the production of better pots, better balanced batches and more careful workings, most of the troubles were eliminated. Before some of the plants had pyrometers installed, their workers guessed at the temperature—and the result was a guess in colors. Most of the colored glasses are now brought up to a melting temperature of 2450°F, with a working range of about 1800° to 1900°F.

The glass blowers employed were from window glass houses. Sometimes the glasses were blown into cylinders as is done in ordinary window glass, and the flattening and annealing also were the same as in window glass practice.

Process

When the batch is blown into balls a different gathering is required. These balls average about 36″ in diameter. Some of the balls weigh 18 to 20 lbs. The neck, good for cullet, weighs from 4 to 6 lbs., leaving about 14 to 15 lbs. of glass fit for commercial use. The shop would get about 100 to 110 balls out of a pot with a ton capacity.

For some colors and some batches a closed pot is more desirable. The open pot is used whenever possible on account of pot and fuel cost. A great deal of skill was required to get uniform thickness of glass in the large balls. Operators were developed to such a degree of skill that they could blow free hand, balls of almost uniform diameter and shape. One firm tried to blow them into paste molds but this was too slow and expensive and did not improve the quality.

From these balls the goggle lenses are cut in various ways depending on the ingenuity of the operator in charge. Special annealing is not required.

The circles are now called mi-coquille lenses. As the surfaces are practically concentric, they answer the purpose for eye protection—not correction. The coquille lenses are cut from balls 12 to 18 inches in diameter. These lenses are not very desirable on account of the irregular surfaces and glass defects.

The Industry

Today amber, smoke, fieuzal, amethyst, blue, green and other colors are produced in satisfactory shades and colors. E. E. Shreiner names 104 glasses in his work on colored glass, most of which could be grouped into about ten combinations of color.

All of the glass must average from $1^1/_2$ to 2 millimeters in thickness. The shades range light, medium and dark. The light shade is divided into 1 and 2, the medium into 3 and 4, the dark into 5 and 6. Extra dark shades such as 7, 8, 9 and 10 are for industrial or special purposes.

The colored goggles on the local market are now fitted with American made glass. One Pennsylvania firm made more than a million pairs of colored goggles for the Allied and United States Armies. These goggles are used for eye protection of truck drivers, aviators, ambulance drivers, lookouts on ships, anti-air craft corps, industrial workers in military repair shops, troops in snow clad countries, ship builders, welders, riveters and every conceivable occupation.

The subject of eye protection has become so important that codes covering the variety of glasses for the several industrial uses have been adopted.

The development of ophthalmic glass for eye correction has had this same sort of development, prompted at first by necessity and now continued on a large production basis.

To the glassmaker who takes up the subject scientifically and produces glasses with known power of absorption and transmission on a commercial basis the field is unlimited.

The coloring agents were easy to secure; the big secret was a batch of balanced chemical composition. Formulae were readily obtained, but the old glassmaker could not understand why iron gave an orange color with one batch and dull green with another. Oxidizing and reducing flame meant nothing to him—he usually wanted heat and the pots to stand the heat.

TYPE OF FORMULAE USED

Batch Used for Medium Amber

Sand	600 lbs.
Soda Ash	200 lbs.
Barium Carbonate	125 lbs.
Calcium Carbonate	48 lbs.
Nitrate Soda	48 lbs.
Red Iron Oxide	65 lbs.
Manganese	48 lbs.

For fieuzal—a yellow green—they used bichromate potash (8 oz.) and black oxide nickel (4 oz.) to 100 pounds of the base batch.

BROWN: Nickel and Mixture Manganese and Iron Oxide

AMBER: Sugar, Coal, Carbon, Red Oxide Iron or Sodium Uranate, Charcoal, Saltpetre, Salt, Charcoal, Tartar, Calcined Oats

SMOKE: Combination of Red Iron Oxide, Manganese, Copper or Black Oxide Nickel

WHITE OR OPAL: Phosphate of Lime, Talc, Cryolite, Alumina or Zinc Oxide, Calcium Fluoride

BLACK: Cobalt Oxide, Nickel Oxide, Iron, Platinum, Iridium, or Basalt, Iron Ores

YELLOW: Uranium, Carbon in various forms, Potassium Antimoniate, Sulphur, Ferric Oxide, or Silver Nitrate, Cadmium Sulphate, Vanadium, Cerium

RED OR RUBY: Red Oxide Copper, Selenium, Gold Chloride, Purple of Cassius, or Antimony Oxysulphide, Manganese, Oxide Iron

AMETHYST OR VIOLET: Manganese Oxide or Nickel Oxide

BLUE: Cobalt Oxide, Nickel Oxide, Iron Oxide or Copper Oxide

GREEN: Chromium Oxide, Black Oxide Copper, Red Oxide Iron, Vanadium

Rare earths have not been considered in this paper. To those interested the author suggests J. Newton Friend's "Inorganic Chemistry," Volume IV, on "Aluminium and Its Congeners—including Rare Earth Metals."

Reading, Pa.

A NOTE ON EARLY OPTICAL GLASS MAKING IN THE UNITED STATES[1]

By Henry H. Blau

ABSTRACT

The manufacturing process employed and the products obtained in the early work on optical glass in the United States, are described in detail.

Contrary to general belief, optical glass was manufactured in the United States as early as 1888. After our entrance into the World War, no less reliable a periodical than the *Literary Digest* published the statement, "Not an ounce of optical glass was made in the United States before the war." However, in April, 1917 the investigations of the National Research Council revealed that such information was incorrect, and Arthur L. Day representing that body states in his paper, "Optical Glass and Its Future as an American Industry," "It is to the credit of the elder Macbeth of the Macbeth-Evans Company, that the first attempt to manufacture in this country glass of high optical quality was undertaken in the early nineties and a number of creditable lenses, some of considerable size, stand as monuments to the success of this effort." Under the belief that a brief review of this work would be of general interest, information concerning this early venture was collected and the present paper undertaken.

John A. Brashear, the noted manufacturer of astronomical apparatus, was a close friend of George A. Macbeth. Through Dr. Brashear, Mr. Macbeth became interested in the superior quality of glass imported from abroad and used in the Brashear Laboratories. This interest became an enthusiasm, and in 1888 Mr. Macbeth decided to attempt the manufacture of optical glass. At that time he was operating a factory known as the "White House," located on the South Side in Pittsburgh, where he produced lamp chimneys and some glass dials for watches, from a lead glass of a quality superior to that previously produced. A few blanks were pressed from it for Dr. Brashear. It was not until 1889, however, that the commercial manufacture of optical glass was really undertaken, and a plant for this particular purpose constructed in conjunction with his new works at Elwood, Indiana under the supervision of T. F. Harnack, now of the H. L. Dixon Company but formerly superintendent of the Macbeth Factory at that place.

In accordance with the custom of those days, this plant was given a name, "The French House," derived from the nationality of its manager, Eugene Field. Mr. Field came from a line of optical glass makers, and had followed this work in Europe with his father, the maker of the Lick Observatory lens. With his knowledge of foreign methods and Mr. Macbeth's of the American glass industry, the proper materials were obtained and methods established for the production of optical glass of the extremely high quality required for scientific apparatus.

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[1] Presented at the Atlantic City Meeting, Feb., 1924 (Glass Division).

The purest materials available were used in the making of this glass. The sand was shipped in barrels to Indiana from the Berkshire Hills of Massachusetts. The sodium carbonate was of the grade known as Sullivan ash 58% and was imported from England in casks. The potash and barytes were obtained from Germany in similar containers, and the niter from Chile. The litharge was purchased domestically until its manufacture was undertaken at Elwood to obtain material of satisfactory purity. The soluble materials were purified by dissolving in water, removing the scum and crystallizing them out of the solution after decantation into an evaporator. Satisfactory barrelled borax was obtained in this country. These materials were introduced into the glasses in varying proportions.

The inability to locate all of Mr. Macbeth's records together with the jealous secrecy of those times precludes a detailed account of the development of the compositions used. It is known, however, that crowns, flints, barium crowns and barium flints were made. Batches for these glasses together with corresponding cullet were filled into a one-pot furnace.

The old "French House" had but a single one-pot furnace, a deep-eyed one, fired by natural gas. It consisted of a chamber ten feet square inclosed by refractory brick walls eighteen inches thick and four feet high, surmounted by the ordinary crown and stack. The bench was built up of the glass house refractory brick used in those days. The pot was placed in the furnace so that its rear wall abutted on the eye. These pots, as well as the clay molds used in reforming the glass, were manufactured by the Willetts Company, which then maintained a pot house at Elwood, Indiana. They were covered, 22 inches in diameter and accommodated a metal depth of about 16 inches. They were placed in the furnace and gradually heated up to melting temperature when they were charged with a mixture of batch and cullet.

The manufacturing process was much like that of the present day. After the contents of the pot were completely fused, a preheated clay stirring rod was introduced through the pot mouth. An iron handle supported by chains from a roof truss was fitted inside the clay stirrer, and with this arrangement the glass was stirred with a circular motion for from six to eight hours. When proofs indicated that the glass was homogeneous, the gas fire was slowly turned down and the stirring continued until the glass became too stiff to permit it. All openings to the furnace (including the stack) were then sealed, the gas turned off, and the furnace and its contents allowed to cool gradually.

When completely cooled the pot was removed from the furnace and the clay broken away from the glass. The fragments of glass as well as the imperfect larger pieces were discarded as cullet, and those larger ones found to be free from imperfections, were subjected to further treatment.

Pieces of a weight approximating that desired in the finished article were placed in chalk-covered clay molds whose shapes were plane, convex or concave depending on requirements. These molds containing the glass were placed in a reheating furnace eight feet square on the inside, bounded by eighteen-inch walls and fired from two opposite sides with natural gas. Heating was continued until the glass had softened sufficiently to conform to the shape of the mold. Then, after sealing the oven tightly, the gas was turned off, and the glass cooled in the oven very slowly. The cooling rate depended on the size of the pieces, the larger ones requiring as high as four days.

Those pieces which had not melted down sufficiently were placed in the remelting furnace again and the others were tested for freedom from strain with a polariscope and their densities checked. Some of the smaller pieces were shaped by reheating and placing in a press. These had to be subsequently annealed in a kiln.

"The French House" was provided with small grinding and polishing units so that test pieces were made on the ground. This testing work was sufficiently well correlated with the composition of the glass that Mr. Macbeth was able to obtain lens blanks to replace several imported ones broken in grinding, when Dr. Brashear was constructing the six-inch lens system for the telescope of the University of Tokio.

This was but one of the notable installations in which the optical glass produced in "The French House" was used. Blanks made at Elwood were also used by Dr. Brashear:

1. For the photographic corrector in the twelve-inch objective for the Dudley Observatory of Albany, New York.
2. For a triplet for the Dr. Gill National Observatory of South Africa.
3. For the six-inch aperture lens for the astronomical photography camera of Princeton Observatory.
4. For the two-inch spectrographic lens of the University of Chicago.
5. For a range finder objective manufactured March 15, 1898.
6. For a six-inch lens of 400 feet focal length for the U. S. Army Signal Corps.

Dr. Hastings of Yale University tested Macbeth prisms in January, 1892 and at that time found a crown one to have a dispersion of 0.0188 for the B and C lines. The same year he used a flint glass in making a 9.25-inch objective for that Institution. Bausch & Lomb and the Eastman Kodak Company also purchased some glasses, including a lead one of the high density of 3.58. During the International Exposition held in Chicago in 1893, Mr. Macbeth was awarded for his exhibit of optical glass-discs, a diploma, which reads:

"Optical Glass: In this exhibit are shown disks of Crown and Flint Glass of the following diameters: 3, 4, 5, 6, 8, 12, 16 and 23 inches, of which one, 12 inches is of Flint and one of Crown. The specific gravity of the Flint is 3.50 and of the Crown 2.51. The two latter together with a $5^1/_2$ Flint prism are the first of their respective sizes of American manufacture ever exhibited. In freedom from bubbles and stones they are of a high grade."

All of this goes to show that optical glass of high quality was manufactured in the United States many years ago on a successful basis. In spite of the perseverance of those engaged in the work the effort was doomed to commercial failure, because the big users could not be weaned away from the foreign sources of supply and no market could be found for the smaller pieces. The manufacture was finally abandoned for these reasons.

Charleroi Laboratories
Macbeth-Evans Glass Company

FACTORS AFFECTING THE WARPAGE OF SHEET IRON AND STEEL IN ENAMELING[1]

By R. R. Danielson, T. D. Hartshorn and W. N. Harrison

ABSTRACT

The effects upon warpage of different methods of cleaning the metal, durations of firing periods, scaling practices, gages of metal, types of enamel, etc., are studied. Test pieces 16 x 16 inches are employed, several commercial enameling irons and steels being used and compared. Warpage is determined by obtaining the areas on five evenly spaced, vertical planes, parallel to one edge of the test piece, included between a flat, horizontal base plane and the contour of the test piece resting thereon. The average of the five areas in square centimeters is used to express numerically the degree of warpage.

The conclusions are: (*a*) A wide divergence between the expansivities of the enamel and the metal base induces warpage, (*b*) there seems to be less tendency for the scaled metal to warp than for that cleaned chemically, (*c*) thin metal is more sensitive to the factors affecting warpage than thicker metal, (*d*) sudden, irregular cooling induces warpage, (*e*) tendency to warpage is reduced by properly supporting the ware during firing and cooling.

Introduction

The warping or buckling of sheet iron and steel during the enameling process is a cause of considerable loss and worry to the manufacturers of flat ware, such as stove parts, table tops and signs. An investigation was undertaken by the Bureau of Standards, in coöperation with the Enamel Division of the American Ceramic Society, in order to obtain definite information on this important subject.

The problems bearing upon warpage may be divided into two general classes; those which are essentially metallurgical, and those which are related to the practices and materials used in application of the enamel. The use of only such conditions as could be practically reproduced with the equipment ordinarily found in enameling plants was planned for this investigation, and consequently, although factors of both classes are involved in many steps of the enameling process, the investigation was directed primarily upon those of the non-metallurgical type, except that iron and steel from several sources were used, and their warpage compared. The effects of various methods of cleaning the metal, methods of scaling, time of firing, and other factors having a bearing on this problem were also studied.

Materials

The sheet iron and steel used in this investigation were received from three manufacturers, and are designated as metals A, B, and C. All of the sheets received from each manufacturer came from the same melt, with the exception of lot B, which contained an extra set from a different melt, designated as metal B′. Metals A and C are commercial enameling irons, while B and B′ are commercial steels. Metal B is a rephosphorized basic, open-hearth steel, and B′ is a low phosphorus basic, open-hearth steel.

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[1] By permission of the Director, Bureau of Standards. Presented at the Atlantic City Meeting, Feb., 1924. (Enamels Division.)

Each manufacturer furnished sheets of rolled stock, 96 by 32 inches, in both 18 and 22 gages. There were 12 sheets each of metals A, B and C, six in each gage. Metal B′, however, was furnished in only 18-gage, giving a total of 42 sheets from all sources. The sheets were numbered A-1, A-2, ——, B-1, B-2, etc. Each of these sheets was cut into 12 plates, 16 by 16 inches, which were numbered as illustrated in Fig. 1, making a total of 504 test plates. Each plate was stamped with its number for easy identification. Thus plate B-10-9, shown in Fig. 2 was cut from position 9 (Fig. 1) of sheet B-10.

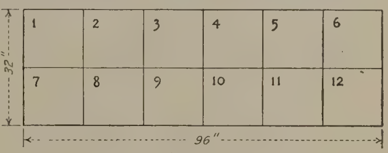

Fig. 1.

The system of numbering the plates was the same for each sheet in order to trace the history of each test plate, not only with regard to its location in each sheet, but also as to the method of handling the individual plates.

Three ground and three cover enamels, covering a wide range of expansivity, were prepared according to the compositions in Table I. The batch compositions are shown in Table II.

In order to obtain uniform results, a sufficient quantity of each enamel was obtained from a 300-pound batch which had been melted in a commercial smelter. All were milled in 100-pound lots to pass a 60-mesh sieve for the ground coats and 80-mesh for the cover. The ground and cover enamels designated as L (low expansivity) have a coefficient of expansion decidedly below that of iron and steel, which is usually given as 12×10^{-6} to 13×10^{-6} per °C (linear), and are comparatively refractory. Enamels M (medium expansivity), which are more fusible, have a coefficient of expansion more nearly approximating but still lower than that of the metal, while enamels H (high expansivity) have an expansivity approximating that of iron and steel and are fusible at comparatively low temperatures.

Procedure

The enamels were applied by dipping, each plate being ground-coated on both sides and given two coats of the cover enamel on the numbered or top side. It should be noted that some plates were later given third and fourth applications of the cover coat as more than two are not unusual in sign work.

The plates were burned in a two-burner, gas-fired muffle furnace, having a muffle chamber 20 x 48 inches. Temperatures were measured with a platinum-platinum rhodium thermocouple which extended 8 inches within the muffle. The standard support used in firing consisted of seven parallel rows of eight points each, composed of a heat-resisting alloy. This arrangement gave each plate uniform support. Each piece was removed from this rack with a steel fork and allowed to cool upon a cast iron grid or cooling table of the open webbed pattern.

TABLE I

ENAMELS

Theoretical melted compositions

Enamel	Feldspar, per cent	Boric oxide, per cent	Cryolite, per cent	Sodium oxide, per cent	Fluorspar, per cent	Cobalt oxide, per cent	Observed linear coefficient of expansion
Cover L	60	21	12	2	5	..	9.3×10^{-6}
Cover M	60	15	12	8	5	..	11.7×10^{-6}
Cover H	60	9	12	14	5	..	12.4×10^{-6}
Ground L	60	21	11	3	4	1	9.5×10^{-6}
Ground M	60	15	11	9	4	1	11.2×10^{-6}
Ground H	60	9	11	15	4	1	12.3×10^{-6}

TABLE II

ENAMELS

Batch compositions for 100 lb. melted frit

Enamel	Feldspar, per cent	Boric acid, per cent	Borax, per cent	Cryolite, per cent	Sodium nitrate, per cent	Soda ash, per cent	Fluorspar, per cent	Cobalt oxide, per cent
Cover L	60	37.2	..	12	5.5	..	5	..
Cover M	60	3.0	36.3	12	5.5	..	5	..
Cover H	60	..	24.6	12	5.5	13.6	5	..
Ground L	60	37.2	..	11	5.5	1.7	4	1
Ground M	60	..	41.0	11	6.1	..	4	1
Ground H	60	..	24.6	11	5.5	15.3	4	1

MILL ADDITIONS

Cover enamels		Ground enamels	
Frit	100.0	Frit	100
Clay	5.0	Clay	6
Tin Oxide	7.0	Borax	1
Magnesia	0.5	Water	55
Water	55.0		

The investigation was divided into three sections, a different factor being varied in each. In Section A, different methods of preparing the plates for enameling were used. To differentiate between the two used for removing grease, the terms "cleaning" and "scaling" are employed, the former applying to the use of an alkaline cleaning solution and the latter to removal by a short heat treatment.

Plates 7–12 (Fig. 1), of the first three sheets of each metal, including both 18 and 22 gages, were cleaned, while plates Nos. 1–6 of these sheets were scaled by heating in a furnace at 750°C (1382°F) until the plates reached a dull red color. This selection of specimens insured an equal distribution of corner and middle plates, thus equalizing possible warping tendencies due to position in the large sheet as it was rolled. All were pickled in hot 5% hydrochloric acid, rinsed in water, immersed in a weak soda solution, dried, dipped, and the enamel burned at 875°C (1607°F).

In Section B an attempt was made to determine the effects of variations in firing temperature, 825°C (1517°F), 875°C (1607°F), and 925°C (1697°F) being used. Plates Nos. 5, 6, 8, 10, 11 and 12 (Fig. 1) of the remaining three sheets of each metal were selected and found to be sufficiently free from grease so that they could be pickled without being cleaned or scaled. Only the enamels of medium expansivity were used on these trials.

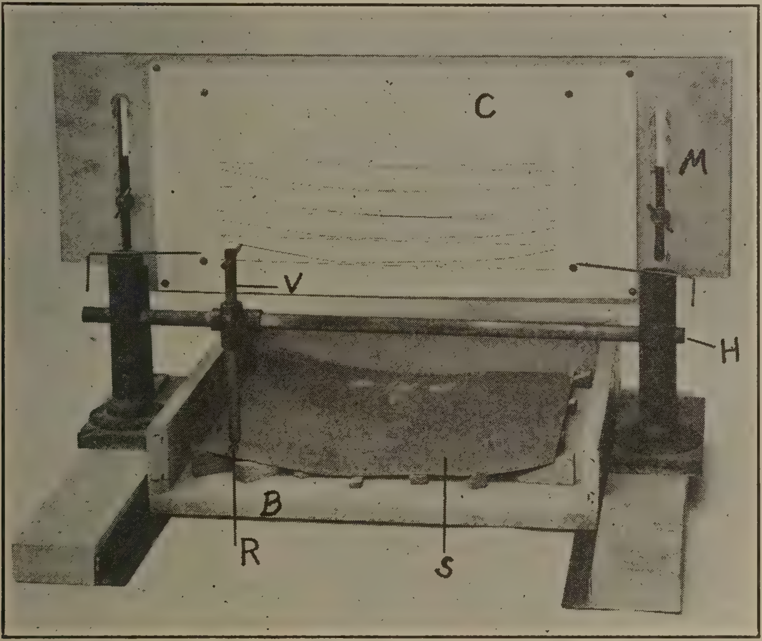

FIG. 2.—Warpage recording device. (The warpage of the test plate shown is 19 units.)

Section C is devoted to the determination of the effect of variation in temperature and length of time of scaling and in the types of supports used for cooling. All the plates not used in the two previous sections were heated at 850°C, 900°C or 950° (1562°F, 1652°F or 1742°F) for periods of two, four and six minutes, respectively, at each temperature. During the scaling operation, a rack of four points, arranged at the corners of an 8-inch square was used. Alternate pieces were allowed to cool upon the same rack or upon the cooling grid. They were then pickled and coated with enamel of the L, M or H type, only the grid being used for support in the subsequent cooling.

Calculation of Warpage

The warpage of the plates subjected to the various treatments was graphically recorded after the ground coat and also after the second cover coat applications. Those receiving four covers were measured after the final coating, and the specimens in Section C, which received special scaling treatment, were measured before being ground-coated.

A photograph of the device used for recording the warpage is shown in Fig. 2. A test plate *S* is placed, concave side up, on the base *B*, movable from front to rear on iron tracks, where it is supported rigidly in its natural position with wooden wedges. The recording chart *C* is attached to board *M*, which slides vertically upon upright bars. The warpage of plate *S* is recorded upon the chart by means of a pencil attached to the vertical rod *V*, which follows the contour of the test piece as *V* is moved along the horizontal rod *H*. Motion upon the plate is facilitated by a small roller *R* on the lower end of rod *V*. Five horizontal lines drawn on the chart are used as base lines in recording five evenly spaced contour curves for each plate. One inch from the rear edge of plate *S*, the roller *R* follows a path which corresponds to the curve over the base line uppermost upon the chart. The plate is then moved by sliding base *B* to a point $3^1/_2$ inches to the rear, where a second cross-section is drawn as a curve on the chart, over the next lower base line. The three remaining cross-sections are recorded in a similar manner. For easy comparison the subsequent warpage measurements for the same plate are made upon the same chart.

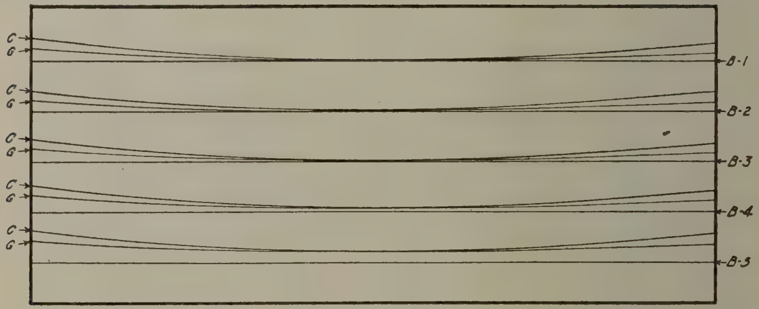

FIG. 3.—Sample chart, showing typical warpage record.

Figure 3 shows diagrammatically the appearance of a sample chart. The curves corresponding to the ground and cover coats are marked *G* and *C*, respectively. The base lines are denoted by *B*. The amount of warpage is an average of the areas between the five base lines and the corresponding contour curves. These areas were determined with an integraph and are expressed in square centimeters. This method takes into account warpage in any direction. Thus, the sample chart shown in Fig. 3 represents a bending up of the plate at the right and left sides, and also the edge next to the observer, since base lines Nos. 4 and 5 are not touched by their corresponding curves. The areas over these base lines are larger as a consequence of warpage in the second direction, and the average area is correspondingly increased.

For measurement each test plate was placed concave side up in order that warpage measurements might be comparable throughout the work.

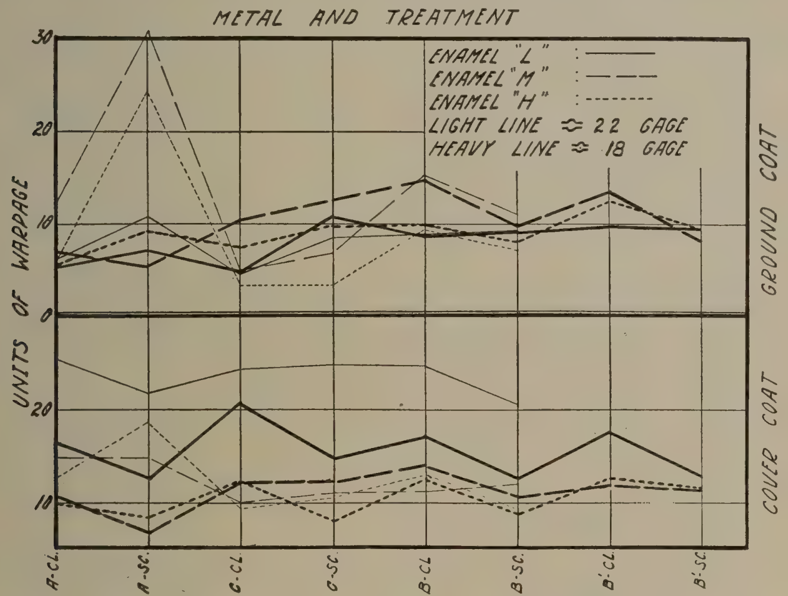

FIG. 4.—Effect upon warpage of method of cleaning metal (Sc. = scaled and Cl. = cleaned).

Results

1. Effect of Variation in Method of Cleaning Metal

The relation between the warpage of cleaned and scaled plates is given in Table III and is shown graphically in Fig. 4. It is appropriate here to explain that in Table III and the corresponding Fig. 4, the high warpage values for the ground-coated A metal of 22 gage, which had been scaled, are believed to be due to the sudden cooling of the plates as they were removed from the furnace, caused by draughts from open windows. This view is based on the contrast between these values and the decidedly smaller ones for those plates which were handled under conditions which were identical except that

TABLE III

AVERAGE WARPAGE MEASUREMENTS FOR CLEANED AND SCALED PLATES. EACH VALUE IS THE AVERAGE FOR 6 PLATES

Units of Warpage

	18 Gage								22 Gage					
	A		C		B		B′		A		C		B	
Enamel	Cl.	Sc.	Cl.	Sc.	Cl.	Sc.	Cl.	Sc.	Cl.	Sc.	Cl.	Sc.	Cl.	Sc.
Ground L	5.3	7.2	4.9	10.8	8.6	9.0	9.8	9.5	6.7	10.9[1]	4.7	8.6	8.9	9.4
Ground M	7.0	5.5	10.4	12.6	14.8	9.8	13.6	8.1	12.0	30.8[1]	5.2	6.9	15.3	11.1
Ground H	5.5	9.3	7.6	9.9	10.0	8.2	12.5	9.4	6.1	24.4[1]	3.5	3.6	9.5	7.4
Cover L	16.4	12.4	20.7	14.8	17.1	12.5	17.6	12.7	25.5	21.8	24.5	24.9	24.8	20.7
Cover M	10.8	6.9	12.2	12.3	14.2	10.6	12.0	11.5	14.9	14.9	10.1	11.1	11.3	12.1
Cover H	9.8	8.5	12.4	8.1	12.5	8.8	12.7	11.6	12.7	18.7	9.5	10.7	13.2	9.4

[1] These values should not be used for comparison with the others in the table, as explained in the text.

TABLE IV

AVERAGE WARPAGE MEASUREMENTS SHOWING EFFECT OF VARIATION IN FIRING TEMPERATURE. EACH VALUE IS THE AVERAGE FOR 6 PLATES

Units of Warpage

		825°C					875°C					925°C				
Enamel	Gage	A	C	B	B′	Av.	A	C	B	B′	Av.	A	C	B	B′	Av.
Ground M	18	5.7	8.5	10.8	10.4	8.9	9.4	10.7	12.1	11.4	10.9	12.6	10.9	10.1	10.4	11.0
	22	3.8	4.8	11.4	....	6.7	7.2	7.0	14.4	....	9.5	17.7	21.5	11.1	....	16.8
				Total Av.		7.8			Total Av.		10.2			Total Av.		13.9
Cover M	18	9.8	11.2	10.4	9.8	10.3	8.6	12.5	9.8	12.8	10.9	8.2	10.9	10.4	12.3	10.5
	22	9.6	9.1	10.0	....	9.6	8.8	11.8	11.1	....	10.6	11.8	13.1	9.8	....	11.6
				Total Av.		9.9			Total Av.		10.7			Total Av.		11.0

the draughts of cold air were eliminated during the cooling. These high values should not be considered in comparing the effect of the other factors upon warpage. A study of Table III and Fig. 4 shows that the effect of method of cleaning varied with the type of metal treated. Thus, for the steel (metals B and B′) we find that the scaled plates are warped distinctly less than the cleaned plates either 18 or 22 gage, and this is true both after the application of the ground coat and after the ware is finished. Considering the iron (metals A and C), we find, on the other hand, that the tendency is for the cleaned plates to be warped less after being ground-coated. After application of the cover coats the results for the 18-gage iron stock agree well with those for the steel, the scaled plates showing less warpage. The warpage values for 22-gage iron after receiving the cover coats, although not entirely consistent, are, with one notable exception, also in favor of the scaling treatment. Since the manufacturers are concerned chiefly with the condition of the finished ware, it may be said that the results of this investigation indicate that scaled metal shows less tendency to warp than cleaned metal.

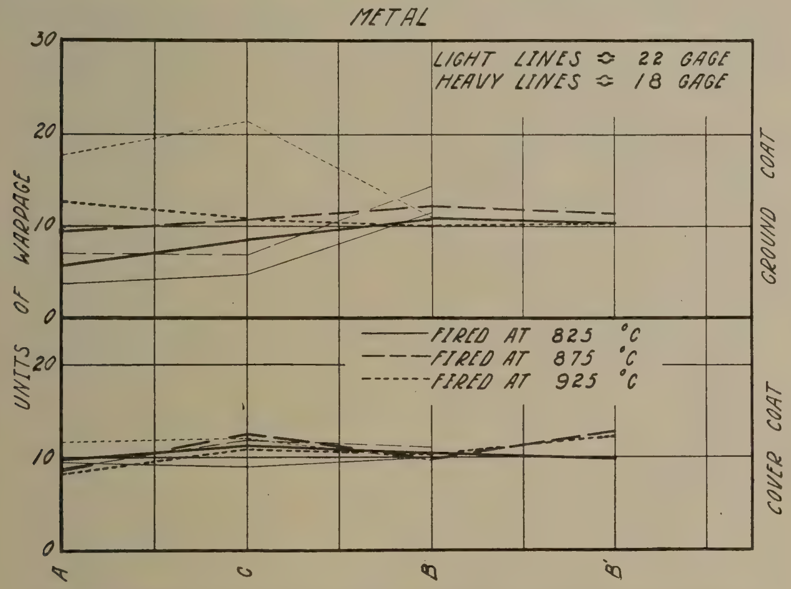

FIG. 5.—Effects of variations in firing temperature, and type and gage of metal, for both ground coats and cover enamels.

2. Effect of Variation in Firing Temperature

Figure 5 shows graphically the relation between the warpage values of plates fired at 825°C, 875°C, and 925°C (1517°F, 1607°F, and 1697°F), respectively. A tabulation of the warpage values is found in Table IV, with the time for firing shown in Table IV-a.

TABLE IV-a

BURNING TIME FOR TABLE IV

	18 Gage			22 Gage		
Enamel	825°C	875°C	925°C	825°C	875°C	925°C
Ground M	4′–45″	3′–5″	1′–50″	4′–15″	2′–35″	1′–25″
Cover M	1′–35″	1′–20″	1′– 5″	1′–10″	–55″	–45″

TABLE V—CORRESPONDING TO FIGS. 6 AND 6-a

AVERAGE WARPAGE MEASUREMENTS FOR PLATES RECEIVING VARIATION IN SCALING TREATMENT. EACH VALUE IS THE AVERAGE FOR 3 PLATES

Units of Warpage

	18 Gage								22 Gage					
	A		C		B		B′		A		C		B	
	P	G	P	G	P	G	P	G	P	G	P	G	P	G
Scaled at 850°C	18.6	4.0	19.2	9.0	17.7	8.8	16.4	7.6	32.6	16.5	34.7	10.1	33.6	7.6
Scaled at 900°C	29.5	12.7	15.8	11.7	27.1	11.5	20.1	8.2	46.6	11.8	40.5	11.7	38.3	6.4
Scaled at 950°C	21.0	10.6	27.9	15.6	25.1	10.3	30.4	4.8	32.1	12.0	26.2	11.5	28.4	7.7
Coated with Ground L	10.9	8.4	6.0	8.7	9.0	11.1	7.4	8.4	9.0	9.1	8.4	10.0	14.1	14.6
Coated with Ground M	12.6	9.2	9.5	11.5	10.8	10.1	11.3	10.2	12.1	12.5	12.2	8.5	14.0	10.3
Coated with Ground H	17.0	7.2	20.2	11.1	9.6	12.1	9.5	12.0	8.4	10.0	11.5	8.6	11.8	10.4
Coated with Cover L	19.8	18.1	19.1	17.3	16.5	16.6	13.8	13.0	23.4	23.9	27.3	19.4	19.3	22.3
Coated with Cover M	14.8	11.6	13.5	14.1	11.7	11.2	14.9	14.5	13.8	12.2	16.6	10.8	12.4	12.7
Coated with Cover H	21.1	12.2	23.4	16.3	15.2	14.8	13.2	16.7	15.2	16.9	16.0	16.7	14.5	13.5

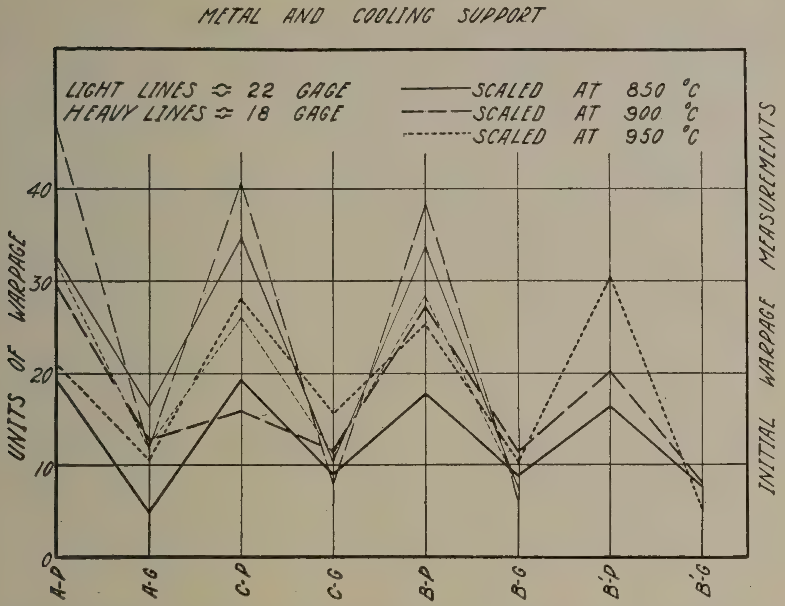

FIG. 6.—Effect of scaling temperatures and type of cooling support on warpage before enameling.

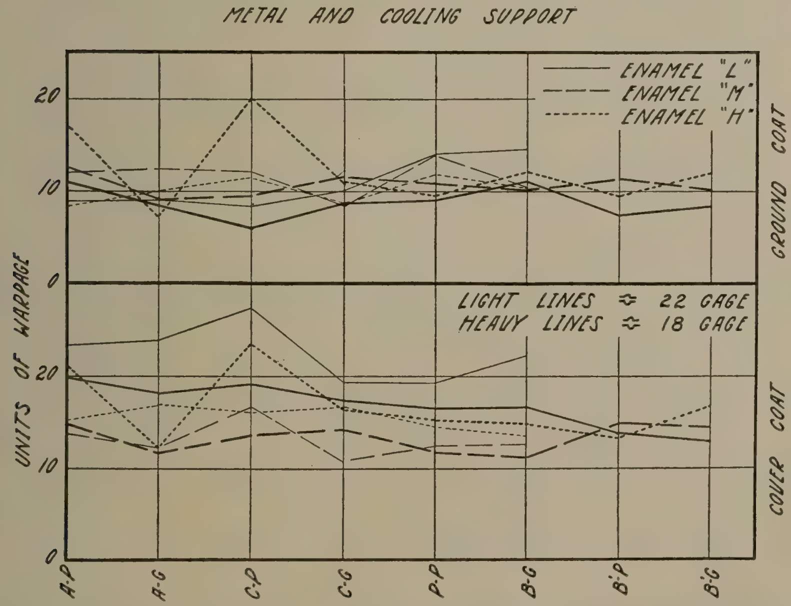

FIG. 6-a.—Effect of variation in support during scaling on warpage during enameling.

Here also, in discussing the effect of firing temperature upon warpage, a distinction must be made between the iron and the steel used in this work. This difference is most noticeable in the ground-coated 22-gage plates, which, in the case of iron (metals A and C), show a very marked increase of warpage as the temperature increases, but for steel (metals B and B′) show about the same warpages at the three temperatures. The 18-gage plates, as might be expected, are affected to a smaller extent, but otherwise the same relation as obtained for the lighter gage holds true.

The effect of variation in firing temperature is consistent and decisive for the ground-coated plates, but has a tendency to become more or less obscured in the subsequent handling and firing accompanying the application of two cover coats. Thus, while the cover coat values do show up in agreement with those for the ground coats in many cases, they seem to be sufficiently obscured to prevent any positive interpretation. The small effect shown for the cover coat may be partially due to the relatively short firing time, and to other factors which become operative, such as the relieving of strain which undoubtedly takes place in a warped plate upon subsequent firing.

3. Effect of Variation in Scaling Treatment

a. The relative effect of the four pins arranged in an 8″ square, and the iron grid, as cooling supports, is shown graphically in Figs. 6 and 6-a, and in tabular form in Tables V and V-a. Table V-a is obtained by condensing Table V.

TABLE V-a

EFFECT OF SCALING TREATMENT ON WARPAGE

	Units of Warpage		
Cooled on	Initial measurement	Ground-coated	Cover-coated
4 pins	28.9	11.3	17.0
Grid	9.8	10.2	15.6

It should be understood that the pins, representing poor cooling support, were used only for the scaling treatment, and that the ground- and cover-coated plates were cooled on the grid in the usual manner. In Fig. 6-a, therefore, the letters P and G (pins and grid) refer only to the type of cooling support used for the scaling process, and similarly in Tables V and V-a the types of support indicated apply only to the initial treatment. In this way the effect of initial warpage of the metal could be traced through to the finished ware.

It is apparent from Table V that the plates cooled on pins after scaling were warped much more than those cooled on the grid, but this is not at all pronounced after the application of the enamels. This is another example of the tendency for the effect of one factor upon warpage to be modified in the successive processes of enameling the ware.

b. The effect of time of scaling is also graphically illustrated in Fig. 7. Table VI, compiled from the averages of values shown in Fig. 7, shows the relative effect of 2-, 4-, and 6-minute scaling periods upon the plates before enameling and after firing the ground coat and the cover enamels.

From this table it can be seen that the warpage for the longer scaling period is greater at the initial measurement. This is quite true of the plates cooled on the regular grid, which furnished normal and adequate support. Here again the effect diminishes with further handling so that the values for ground- and cover-coated sheets show only small, somewhat inconsistent differences. This is true for 18- and 22-gage stock, although the 22-gage metal cooled on the 4 pins, as might be expected, showed more warpage at the initial measurement than the corresponding 18-gage.

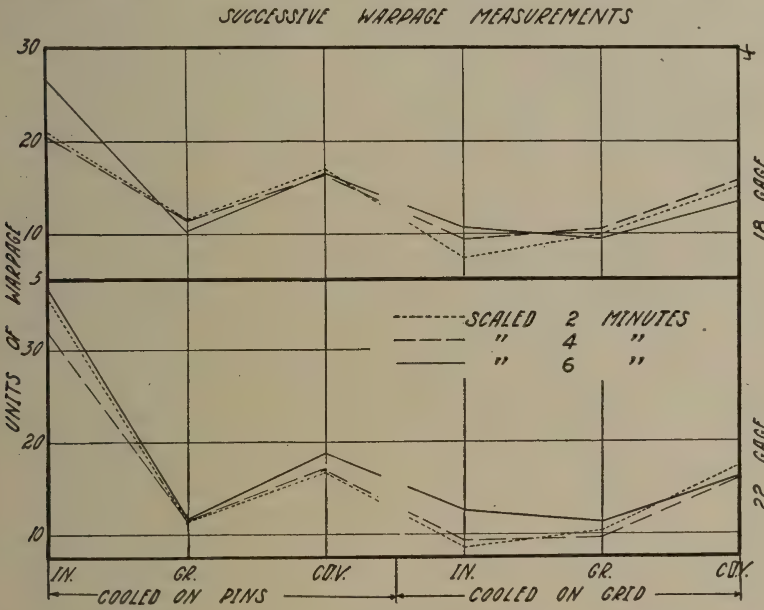

FIG. 7.—Effect of time of scaling and cooling support on warpage before enameling, after ground coating and after cover coating. (IN. = initial, GR. = ground coat, and COV. = cover coat.)

4. Effect of Variations in Expansivity of the Enamels

In a discussion of the effect of the expansivity of enamels upon warpage it should be borne in mind that the metal plates without enamel, when subjected to the heat treatment that they would receive if an enamel were being applied, tended to warp upward at the edges.

A cover enamel applied to the top side only, having an expansivity greater than that of the metal base, would be expected to increase the tendency of the test piece to warp upward, while one having a coefficient of expansion less than that of the metal base should produce the opposite effect. When the application is on both sides of the sheet, as in the case of the ground coats in this investigation, there is some effect upon warpage, but obviously this is not as great as when the application is on one side only.

TABLE VI

AVERAGE WARPAGE MEASUREMENTS SHOWING EFFECT OF VARIATION IN TIME OF SCALING

	Units of Warpage					
	Plates cooled on pins			Plates cooled on grid		
Time of scaling in minutes	Initial measurement	Ground-coat measurement	Cover-coat measurement	Initial measurement	Ground-coat measurement	Cover-coat measurement
2	28.3	11.4	16.7	7.9	10.1	16.1
4	26.2	11.8	16.5	9.3	10.1	15.7
6	31.6	10.8	17.7	11.8	10.3	15.7

A basis for comparing the warpage values of plates coated with enamels of varying coefficients of expansion is afforded in the following data: Table III and Fig. 4 dealing with comparative methods of cleaning (Sec. A), and Table V and Fig. 6-a dealing with variation in scaling treatment (Sec. C). A study of these tables and diagrams indicates that enamel L produces, on the average, somewhat less warpage for ground-coated plates than the M and H enamels. For the cover coat, however, which was applied to only one side, enamel L entirely overcame the tendency of the plates to warp upward, and produced in the opposite direction a warpage which decidedly exceeded that observed in the plates coated with enamels M and H. In section C the warpage of the finished plates coated with enamels H was greater than that of the plates coated with enamels M, although in section A this was not the case.

The direction of warpage, in accordance with the above theoretical discussion, was strongly influenced by the expansivity of the enamel, being away from the enamel on every plate coated with enamel L, toward the enamel on most of the plates coated with enamel H, and irregular on the plates coated with enamel M.

It is interesting to note here that ground coat L displayed a marked tendency to fish scale, while enamels of high expansivity tended to craze although the results which corroborate this statement are not tabulated in this report.

5. Effect of Variation in Source of Sheet Metal

Figures 4, 5 and 6-a constitute a graphical means for comparing the warpage undergone by the metals obtained from the different manufacturers. A condensation of the values indicated in these figures is given in Table VII, which shows the warpage values obtained in each of the three sections of the investigation.

From this table it is apparent that there is no marked difference in the warpage of the finished ware which can be attributed to the source of metal, when all factors affecting warpage are allowed to operate. Certain specific factors, however, seem to affect the iron and steel used in this investigation differently. It will be recalled that method of cleaning affected the steel and iron in somewhat different ways. Also from Fig. 5 it may be noted that metal B (steel), especially for the ground coat, seems less affected by variations in firing temperature than metals A and C (iron). Thus at 825°C (1517°F) the iron is warped less than the steel, while at 925°C (1697°F) the steel has not changed, but the warpage of the iron has increased sufficiently to exceed that of the steel. It should be pointed out that this difference in behavior might be due to factors other than differences in chemical composition of the iron and steels, because different metallurgical processes produce different physical properties in metals of the same composition. It is quite possible, therefore, that specimens of sheet iron and steel manufactured under different conditions might give different results.

6. Effect of Variation in Gage of Metal

Figures 4, 5, 6 and 6-a also take into account the difference between the 18- and 22-gage metal. It is at once apparent from any of these diagrams, or the corresponding tables, that most of the highest warpage values and some of the lowest correspond to 22-gage metal. This fact is interpreted to mean that 22-gage metal is more sensitive to the factors affecting warpage than 18-gage. That is, if a given factor were allowed to operate upon two plates having an equal warpage, one of each gage, whose only difference was one of thickness, the 22-gage plate would be affected to a greater extent than the 18-gage plate, whether the factor in operation tended to increase warpage or to decrease it. This point is brought out especially well in that part of Fig. 5 which deals with the

TABLE VII

AVERAGE MEASUREMENTS SHOWING EFFECT OF VARIATION IN METAL UPON WARPAGE. EACH VALUE IS THE AVERAGE FOR 36 PLATES

		Units of Warpage											
		Average values from Table III (Sec. A)				Average values from Table IV (Sec. B)				Average values from Table V (Sec. C)			
Enamel	Gage	A	C	B	B′	A	C	B	B′	A	C	B	B′
Ground	18	5.9	9.4	10.1	10.5	9.2	10.0	11.0	10.7	10.9	11.2	10.5	9.8
	22	8.3	5.5	10.3	....	9.6	11.1	12.3	....	10.2	9.9	12.5	....
Cover	18	10.8	13.4	12.6	13.0	8.9	11.5	10.2	11.6	16.3	17.3	14.3	14.4
	22	18.1	15.2	15.3	....	10.1	11.3	10.3	....	17.6	17.8	15.8	....

ground-coated plates. Here metals B and B′ show but slight effect in either gage from the factor being varied, and therefore their warpage values do not concern the point under discussion. The warpage of metals A and C, however, is plainly affected by variations in firing temperature, and in the case of both metals the 22-gage plates give both the upper and lower extremes of warpage values. A study of Tables III, IV and V shows that on the whole the warpage of the 18-gage finished ware was less than that of the 22-gage.

Accurate measurements of the gage of each individual plate did not show sufficient variation to appreciably affect results.

7. Effect of Two Extra Cover Coats The warpage values obtained after the application of the second and fourth cover coats did not produce noteworthy changes in warpage, and the results obtained are therefore omitted in this report.

Conclusions

The results of this investigation show that a number of factors have a bearing on the warpage of sheet iron and steel in the enameling process. It is believed that the results are as consistent as might be expected in an investigation conducted on the scale of this study and which has to deal with a large number of factors, all of which appreciably influence results. The data obtained would seem to justify the following conclusions, bearing in mind that while the various factors dealt with appear to be important, some of their effects may be partially or entirely obscured in the finished ware, due to the fact that some of them become fully operative only in the later steps of the enameling process and may tend to nullify the effects produced in preceding stages of manufacture.

1. The application of a cover enamel having a coefficient of expansion widely divergent from that of the metal base decidedly increased warpage in the finished ware, upon which the enamel was applied to only one side.
2. Finished plates from which the grease had been burned preparatory to enameling (scaled) showed less warpage on the whole than those from which the grease had been removed chemically (cleaned).
3. The lighter gage metal, as might be expected, was more sensitive to the factors affecting warpage.
4. The iron base used in this investigation appeared to be less liable to warpage from ground coating at the lower temperatures employed for enamels, while the steel apparently developed less warpage at the higher temperatures. It is pointed out that this might be a special case for these particular lots of metal.
5. Sudden and irregular cooling of the ware after firing induced warpage.

6. The tendency to warp was reduced by properly supporting the ware during firing and cooling.

Summary

It is believed that this investigation, which is regarded as being of a preliminary nature, furnishes data which will be useful as a basis for further investigation. A study of the results suggests that metallurgical factors have a considerable influence on the warpage of sheet metal in the enameling process, and it is evident that a complete solution of the warpage problem must include a consideration of such factors. Specifically, it is suggested that any further investigation upon this subject could profitably include the effect upon warpage of a reduced and controlled rate of change of temperature and a uniform heat distribution for the scaling and firing processes. With these factors under control, opportunity would be afforded to correlate them with and adjust them to the properties of the enamel itself, with a possible beneficial effect upon warpage. A full solution of the problem of reducing warpage to a minimum, then, apparently necessitates working with conditions which could be obtained in the factories only through change in the present enameling practice.

Bureau of Standards
Washington, D. C.

AN APPARATUS FOR MEASURING THE ABRASIVE HARDNESS OF GLAZES[1]

By W. J. Scott

ABSTRACT

An apparatus for measuring the resistance to abrasion, or scratching, of glazes and possibly other materials is described. It provides, essentially, for the wearing away of the surface by means of standard cement sand, which is allowed to run through a funnel adjusted to deliver a definite amount of sand for a given time interval, and to strike the inclined surface of the test piece after falling a fixed distance. The loss in weight under this treatment is assumed to bear a definite relation to the resistance to abrasion.

Introduction

The resistance of ceramic glazes to abrasion, or scratching, affects their usefulness for most purposes. A means of determining this quality is necessary in order to study the factors which may control it, such as temperature of firing, composition, thickness, etc., and in order to provide data upon which specifications may be based. The ideal test is the actual use of the ware under service conditions, but the time involved, the difficulty in ascertaining what the service really is, and in interpreting the results, make it impracticable for most purposes. A test, to be of practical value to the plant manager as well as to the laboratory investigator, must be rapid, easy to perform, and require apparatus of simple and rugged construction, but which, nevertheless, is capable of measuring small variations in this quality of the glaze.

A number of methods requiring various types of apparatus have been proposed; for example, penetration by a needle under pressure, scratching of needles, the use of abrasive wheels, the sand blast, and rotation in a cylinder with an abrasive sand. Tests using these methods are difficult to standardize. The effect obtained by the scratching of needles depends on the sharpness of the point used, on the pressure, and the manner in which the point is applied to the test piece. Control of such conditions is impossible in a practical way. The sand blast gives a variable pressure and volume of sand, both of which are difficult to control even with specially designed apparatus. The measurement of the depth of penetration with any accuracy, by means of microscope or micrometer, is difficult. An exhaustive study of such methods was not, however, made in this investigation because of the greater promise of the following method developed at this Bureau. It was found that the use of a stream of falling sand gave very consistent results on material of the same kind, and, when several brands were tested, the loss in weight seemed to be a satisfactory index of the relative resistance to abrasion.

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[1] Published by permission of the Director of the Bureau of Standards of the U. S. Department of Commerce. Received Jan. 28, 1924.

Apparatus Used

The complete apparatus now in use is shown in Fig. 1. The opening in the bottom of the sand hopper is set so as to keep the small adjustable funnel beneath it just full of sand. The funnel, shown in detail in Fig. 2, has for its sides two steel plates $5^{5}/_{8}$ inches long, set at an angle of 60° to each other, and capable of sliding in grooves in the thicker aluminum ends, which are $3^{3}/_{4}$ inches apart.

The width of the lower opening can be adjusted to give a definite flow of sand by means of the graduated adjusting screws. From the lower opening of the funnel the sand drops $4^{1}/_{2}$ feet to the surface of the test piece which rests on an adjustable support, capable of vertical adjustment, of being leveled, and of being inclined (at the desired angle of approximately 24°) from front to back.

The specimen is prevented from slipping off the support by thumb tacks pressed into its wooden top, or by any other suitable device.

The abrasive used is standard Ottawa sand, prepared for cement testing by screening to pass a 20-mesh and remain on a 30-mesh screen, and is allowed to fall on each piece at the rate of 64 pounds in ten minutes, the test period used in this work. The test piece must contain a relatively flat area at least $1^{1}/_{2}$ by $4^{1}/_{2}$ inches.

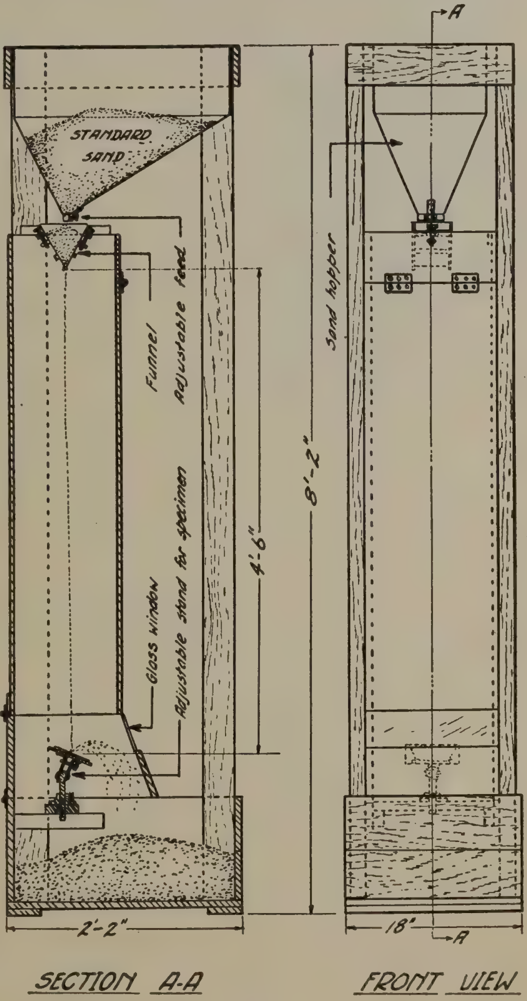

Fig. 1.

The details of construction and operation described above are the result of numerous tests on the effect of type of funnel, height of fall, time of test, and so forth. The standard sand was selected on account of its uniformity. The height of fall is limited by head room for the apparatus, and the spreading of the sand stream as the height increases. Variations in the pressure head of sand are eliminated by the separate hopper.

The funnel as described has the advantage over circular glass funnels which were first used, in reproducibility, and in that the sand grains interfere less with each other in striking the test piece, which produces a greater loss in weight in a given time. The opening of the funnel is made adjustable to permit control of the sand delivered, and to compensate for any possible wear at the opening.

Preliminary tests indicate that the angle at which the test piece is inclined gave greatest cutting action for the same weight of sand, and the test period used is sufficient to produce a satisfactory loss in weight. Further modifications may become necessary when a more comprehensive study of the method and its application is made.

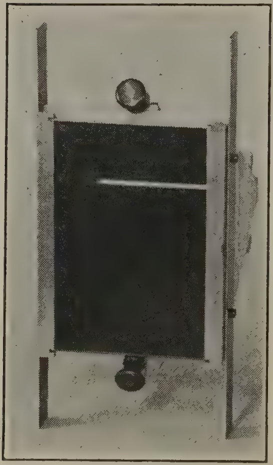

FIG. 2*a*.

Results Obtained

The accompanying table shows typical data obtained on several brands of the common types of tableware and also on plate glass. Trials 1 and 2 in each case were made on pieces broken from the same plate. The loss in weight given is for a 10-minute test on each trial. A larger number of tests may show a different average range between types, brands and specimens, but the brands are thought to be representative, and the results, therefore, indicative of what may be obtained in using the apparatus. The loss in weight may not be proportional to abrasion, but it seems reasonable that a glaze giving a small loss in weight is more resistant to abrasion than one giving a greater loss. Plate glass, because it has greater uniformity than glazes, was found to be useful in checking the performance of the apparatus.

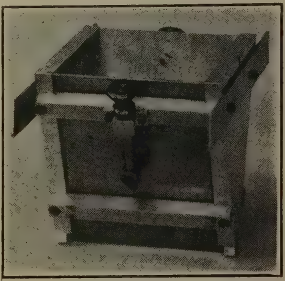

FIG. 2*b*.

TABLE I

Type of specimen	Loss in milligrams	
	Trial 1	Trial 2
Plate glass 1	95	95
Plate glass 2	86	86
Semi-vitreous 1		
Specimen A	93	93
Specimen B	93	92
Specimen C	89	90
Semi-vitreous 2		
Specimen A	65	62
Specimen B	67	66
Semi-vitreous 3	71	72
Semi-vitreous 4	60	60
Vitreous 1	89	89
Vitreous 2		
Specimen A	70	76
Specimen B	68	..
Vitreous 3		
Specimen A	58	59
Specimen B	59	56
High-fire vitreous 1	46	45
High-fire vitreous 2	47	46
High-fire vitreous 3	43	42

Factors Affecting Accuracy

Some factors which must be considered because of their possible effect on the accuracy of the determinations are the wearing of the sand grains, the accuracy of the weighing, the humidity, and the slight curvature of the surface of the test-piece. Occasional checking against a standard material is expected to eliminate the first source of error, although it is believed to be slight for a limited number of runs because a screen analysis of some sand used about 75 times showed that it still passed the test for standard sand, and that the per cent through 30-mesh had increased from 0.36% to 0.86%. The table indicates the value of the method for research work, and also for factory control and other purposes requiring less accuracy. It has not been noticed that either humidity, or curvature of the specimen, introduces errors, but it is intended to check these and other possible sources of error by tests.

Possibilities of the Apparatus

The following observations as to the advantages and possibilities of the apparatus seem justified:

1. The close agreement in results, obtained with test pieces of the same specimen, indicates satisfactory accuracy. This qualification, combined

with simplicity of construction, ruggedness, and ease of operation, make its use possible in plant as well as in research laboratories.

2. It apparently measures small differences existing in glazes of the same brand, and indicates wide variation in glazes of different brands and types.

The author wishes to acknowledge the assistance of R. R. Danielson and other members of the Ceramic Division in the development of the apparatus.

Bureau of Standards
Washington, D. C.

UTILIZATION OF GEORGIA KAOLINS IN THE MANUFACTURE OF FACE BRICK[1]

By R. T. Stull[2] and G. A. Bole[3]

ABSTRACT

The availability of the sedimentary kaolins of Georgia for the manufacture of face brick, when blended with sufficient flux-bearing rock (aplite) and sand, has been demonstrated. Two representative clays were used. Four samples of aplite were mixed with varying amounts of the kaolins and fired to cones 6 and 12. The physical properties of the fired specimens are tabulated. Using this information as a basis, semi-commercial tests were run using varying percentages of kaolin, aplite and sand. Bricks were made up by both the dry press and stiff mud process and fired to temperatures around cone 9. Trouble was experienced due to excessive shrinkage and due to cracking with mixtures containing no sand. Due to lower drying shrinkage, the dry press method of manufacture was found to be better suited to certain mixes than the stiff mud process. A mix was finally produced which went through the stiff mud process nicely, dried safely, and burned to a dense, light buff body at cone $8^1/_2$. The total shrinkage of this body was comparatively low.

Introduction

Throughout the southeast, and more especially in the Coastal Plain States, no clays have been found from which face brick, light cream to clear buff and light gray in color, can be made. Large quantities of such brick are used in this territory for building purposes and substantially all are shipped in from north of the Ohio and Potomac Rivers.

These desirable light colored brick carry a freight charge of $18.00 to $20.00 per thousand, bringing their delivery cost up to about $48.00 to $55.00 per thousand.

Clays in Georgia suitable for the manufacture of face brick of red through brown to gun metal hues are comparatively scarce. These are confined mostly to the variable clays derived from the decomposed granites, to alluvial clays more or less sandy and irregular, and to shales in a small area in the northwestern corner of the state.

The bulk of the cream, buff and gray brick finding their way into the southern market are made from No. 2 fire clays, generally obtained by underground mining. The coal measure clays of the south, and more especially those of Georgia and Alabama, are high in iron and burn to a dark color not at all comparable to the light colored brick made from the fire clays of the Freeport, Mercer and Kittanning formations of Ohio and Pennsylvania. For several years brick manufacturers have been searching the south for clays from which buff and lighter shades of brick could be made. Up to the present time their efforts have not been rewarded.

The geology of the country indicates that no clays are likely to be found which in themselves will produce brick equal to those made from the No. 2 fire clays of Ohio and Pennsylvania. It, therefore, occurred to the senior writer that the best possibility of producing such brick would be to utilize the sedimentary kaolins of the Coastal Plain in a synthetic mixture by adding the necessary fluxes lacking in them.

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[1] Published by permission of the Director, U. S. Bureau of Mines. Presented at the Atlantic City Meeting, Feb., 1924. (Heavy Clay Products Division.)

[2] Assistant General Industrial Agent, Central of Georgia Railway Company.

[3] Superintendent, Ceramic Experiment Station, U. S. Bureau of Mines.

A previous investigation of the sedimentary kaolins of Georgia has shown their high refractory value.[1] Their refractoriness is due mainly to their low content of fluxing impurities. It would, therefore, be impractical to make face brick from these kaolins alone, because the temperature required to burn them dense to vitrified would be too high to attain economically. Even when burned to a vitrified condition, the shrinkage is so great that warping and cracking are excessive.

In the Piedmont Plateau to the north, and bordering the kaolins of the Coastal Plain comparatively large deposits of aplite are found. These deposits occur in dikes and vary from a few feet to over a thousand feet in width. These aplites are composed mostly of mixed feldspars and quartz with very little or no mica. The microscopic examination of several specimens indicates that they are composed principally of orthoclase, albite, microcline and quartz. Their iron content as Fe_2O_3 varies from 0.5% to about 2.0%, and their combined alkali and alkaline-earth content from 6% to 14%.

Chemical analyses of specimens of these rocks from different localities show considerable variation in composition. The rocks are neither pure nor white enough to be useful for high-grade ceramic purposes and in fact no important commercial use has been found for them except the local use of the partly weathered outcrops as road material.

These aplites contain the desirable fluxes lacking in the kaolins, and by mixing them in proper proportions to produce the desired fluxing action and adding sufficient quartz sand (usually found below the clays), to control the shrinkage, good face brick can be made, varying in color from a light cream, light buff to light gray, the color depending upon the iron content in the raw materials and the burning treatment.

The coöperative agreement between the Bureau of Mines and the Central of Georgia Railway Company originally included the investigation of the kaolins, bauxitic clays and bauxites for pottery, fire brick and filler purposes. The possibility of producing a light-colored face brick by utilizing the kaolins, made it possible to extend the coöperative agreement to include this investigation.

Small Scale Tests

The first tests were made with small trial pieces and these were followed by the large scale tests in which full sized brick were made under practical conditions.

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[1] R. T. Stull and G. A. Bole, "Refractory Possibilities of Some Georgia Kaolins," *Jour. Amer. Ceram. Soc.*, **6** [5], 663 (1923).

Aplite Used Preliminary experiments were made to determine the fluxing effects of different aplite samples on Georgia kaolin.

Four different samples of aplite designated as M-1, M-2, M-3 and M-4 were taken from different exposures. Sample M-1 was taken from an exposure where the weathered portion has been removed for road dressing. It was hard, unweathered and dull pink in color. It softened at cone 12 to a light gray porcelain-like glass. The chemical analysis and empirical formula are as follows:

Moisture (at 105°C)	0.02	P_2O_5	0.02
Ignition loss	0.44	CaO	0.54
SiO_2	84.00	MgO	0.11
Al_2O_3	8.93	K_2O	3.13
Fe_2O_3	0.50	Na_2O	2.66
TiO_2	0.02		
		Total	100.37

FORMULA

$$\left.\begin{array}{l}0.376\ K_2O\\0.484\ Na_2O\\0.109\ CaO\\0.031\ MgO\end{array}\right\}\qquad\left.\begin{array}{l}0.988\ Al_2O_3\\0.035\ Fe_2O_3\end{array}\right\}\qquad 15.6\ SiO_2$$

The constitution of the aplite as calculated from the formula indicates that it is composed of the equivalent of approximately: 18.82% orthoclase, 22.83% albite, 6.49% anorthite,[1] 51.86% quartz. No chemical analyses were made of samples M-2, M-3 and M-4. They were partly weathered and somewhat iron-stained in the seams. Their deformation temperatures were cone 12 for M-2 and M-3 and cone 9 plus, for M-4. The color of M-2 and M-3 when fused was light brown while M-4 was apparently more iron stained and fused to a darker color.

Clays Used For the preliminary tests, kaolins G-3, G-8 and G-15 were selected and for the large scale tests, kaolins G-8 and G-35. The chemical analyses and deformation temperature of these kaolins are as follows:

	G-3	G-8	G-15	G-35		G-3	G-8	G-15	G-35
Moisture (105°C)	1.15	1.33	0.74	. . .	P_2O_5	0.05	0.04	0.04	. .
Ignition loss	13.33	12.40	13.79	13.85	CaO	0.39	0.25	0.24	. .
SiO_2	46.56	47.67	43.25	44.26	MgO	0.25	0.37	0.11	. .
Al_2O_3	35.51	35.52	39.45	40.11	K_2O	0.00	0.16	0.16	0.43
Fe_2O_3	1.59	1.26	0.96	0.71	Na_2O	0.00	0.04	0.38	
TiO_2	1.29	1.28	1.17	0.90	S	0.03	0.08	0.15	. .
					Cone	34	34	34+	34+

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[1] For convenience the alkaline earths are calculated as "anorthite" although it is not probable that they occur in that form. The Fe_2O_3, TiO_2 and P_2O_5 are evidently impurities.

All four clays are very plastic and substantially of the same refractory value. G-3 is locally known as a "hard" kaolin as distinguished from a "soft" kaolin. The hard kaolins, when dry, require considerable force to crush by squeezing in the hand, whereas, the soft kaolins are very friable and crumble under a slight pressure. The hard kaolins do not slake readily and require grinding to place them in slip form. They are so fine grained and plastic they clog the filter sacks and make filter pressing next to impossible.

The bonding strength of G-3 is very good. Its iron and titania contents are comparatively high causing it to burn too dark in color for whiteware. It is, however, an excellent material for high grade clay refractories.[1]

Under the above classification, G-8 is known as a "semi-hard" kaolin. It contains occasional fine quartz grains and mica flakes. It slakes and filter presses slowly. It is very plastic and shows good bonding strength. Its color, when burned, is too dark for whiteware, though it is lighter in color than G-3.

G-15 is locally called a "blue clay." It would be classed between the semi-hard and the soft kaolins. It represents the lower 15 to 20 feet of a working mine of 35 to 50 feet in thickness. Its blue color (evidently due to organic stain), is such that it is not a desirable clay for filler purposes. However, it burns sufficiently white to be of value for whiteware.[2] It slakes readily and filter presses slowly. It is very fine grained, highly plastic and has fair bonding strength.

G-35 is decidedly a soft kaolin. It is very white and friable. Although very plastic, it has comparatively low bonding strength. Its alumina content is comparatively high and its iron and titania contents comparatively low. It slakes and filter presses readily and is a suitable paper filler as indicated by tests.[3] It burns to a good white and is mined and shipped crude, principally to the floor and wall tile trade.

Preliminary Tests

For the preliminary tests, G-15 was used in combination with the four different aplites (ground to 65-mesh) and potters flint in mixtures according to the following table.

The mixtures were kneaded into a good plastic condition and the trial pieces molded by hand in the form of two-inch cubes. These were dried and fired to cone 6.

There was comparatively little difference in the appearance of the trials made from the same aplite. Trials containing M-1 were a cream color while those containing M-2, M-3 and M-4 were light buff. All contained a few fine black specks which improved their appearance. The structure of the trials appeared to be good even though their porosities were comparatively high. Trials containing 50 to 55 aplite and 50 to 45 kaolin showed lowest porosity, the average being 19.3%. At cone 6 there appeared to be no marked difference in the porosity of trials containing M-4 as compared to the others even though its deformation temperature was three cones lower.

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[1] Stull and Bole, *loc. cit.*

[2] G. A. Bole and R. T. Stull, "Use of Sedimentary Kaolins of Georgia in Whiteware," *Jour. Amer. Ceram. Soc.*, **6** [7], 854 (1923).

[3] W. M. Weigel, "Georgia Clays for Paper Fillers," *Paper Trade Journal*, August 9, 1923.

GROUP I

No.	G-15	Aplite	Flint
1	55	45	0
2	50	50	0
3	45	55	0
4	50	40	10
5	50	35	15
6	50	30	20

Results of Cone 12 Burn

To produce a vitrified condition and to observe its influence upon the color and general appearance, a duplicate set of Group I was burned to cone 12. Trial pieces were also placed in the kiln to observe the behavior of kaolins G-3 and G-8 in combination with the four different aplites. These mixtures were composed to 50% kaolin and 50% aplite and designated as Group II.

At cone 12, the colors varied from a gray-white in trials containing M-1 aplite and G-15 kaolin to a medium gray in trials containing M-4 aplite and G-3 kaolin. The fine black specks were developed more prominently and gave the trials the appearance not unlike light colored, fine grained granite. To the eye, the structure of the trials appeared dense and well vitrified although the average porosities of the different mixtures varied from about 4% to 14%. The porosity is evidently due in part, at least, to the coarser grinding and coarser structure as compared to true porcelain.

COMPARISON OF AVERAGE POROSITIES OF TRIAL PIECES CONTAINING DIFFERENT APLITES

Aplite sample	Av. porosity, per cent Group I	Av. porosity, per cent Group II	Av. porosity, per cent Groups I & II
M-3	4.61	5.12	4.74
M-1	5.69	5.14	5.55
M-2	7.52	9.37	7.98
M-4	11.35	14.20	12.06

The fluxing values, of the four different aplites as indicated by the porosity determinations, were indicated rather prominently as shown in the following table. Compositions containing M-3 showed lowest porosities, while those containing M-4 were highest. No satisfactory explanation for the lower fluxing value of M-4 is apparent in view of its lower deformation temperature.

Full Sized Brick Trials

For making standard size brick, clays G-3 and G-8 were selected principally because neither was considered good enough for whiteware and because they represented undeveloped properties. Inasmuch as there was not enough of any one sample of aplite left for the full sized brick tests, the remainder of the four aplites from the foregoing tests were mixed and ground to pass 65 mesh. The quantity of M-4 was much in excess of the others. In fact it comprised about $^3/_4$ of the mixture.

Mixtures of each kaolin (G-3 and G-8) and aplite were made consisting of 50 kaolin and 50 aplite. Part of the mixtures were molded "dry press" on a small hydraulic machine. The remainder of the mixtures were tempered to a plastic condition, molded by hand and repressed. The brick were dried and burned to cone 10 and shrinkage and porosity determinations made.

TOTAL LINEAR SHRINKAGE AND POROSITIES OF BRICK MADE FROM KAOLINS G-3 AND G-8 WITH APLITE. BURNING TEMPERATURE CONE 10

	Shrinkage, per cent	Porosity, per cent
G-3 (dry press)	5.00	22.50
G-3 (repress)	7.86	21.70
G-8 (dry press)	4.29	16.40
G-8 (repress)	8.57	16.45

No serious difficulties occurred in the drying or burning. The brick appeared to be of good color and sound structure. The color of the repressed brick was cream-gray while the dry press bricks were gray. Bricks containing kaolin G-8 were lighter in color than those containing G-3. All contained a few fine black specks.

Large Scale Tests

The small scale tests indicated the possibility of making face brick from kaolin and aplite rock, containing sufficient alkalies and alkaline earths to produce the desired fluxing action. The next step in the investigation was the determination of the working properties of such mixtures when molded in regular commercial size dry press and stiff mud machines and to determine their drying and burning behaviors. For the large scale tests, 8 tons of material were shipped to the Hadfield-Penfield Steel Company's testing department at Bucyrus, Ohio, where the tests were made,[1] under the writers' direct supervision.

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[1] The writers are indebted to C. B. Shearer and Davis Brown of the above named Company for their interest and hearty coöperation in the work.

The Clay Used

Two tons each of kaolins G-8 and G-35 were taken from the deposits in a manner to obtain fair average samples. Aside from the fact that both kaolins are very plastic, they differ considerably in other properties. As previously mentioned, G-8 belongs to the semi-hard class. It does not burn to a good white, is not used for pottery or filler purposes but has good bonding strength. G-35 is a soft kaolin, burns to a good white, is sold to both the pottery and filler trades but has low bonding strength.

The Aplite Used

Four tons of aplite were quarried from the same dike from which sample M-3 was previously taken for the small scale tests. The dike extends in a northeast-southwest direction and is cut by the railroad at about right angles, showing an exposure approximately 12 feet deep and about 400 yards in width.

The four-ton sample was taken about three feet in from the face and six to seven feet down from the top. The sample was light pink to cream in color, and although quite hard, it was partly weathered with iron stains and thin films of clay showing in the seams.

Inasmuch as no fine grinding equipment of sufficient size was available, the sample was first shipped to a commercial grinding plant where it was ground to pass 60-mesh, then reshipped to Bucyrus for the tests.

Following are the analysis of an average sample of the ground aplite, the empirical formula and the calculated mineral constitution. Its deformation temperature was cone 10.

CHEMICAL ANALYSIS

H_2O (at 105°C)	0.40
Ignition loss	1.62
SiO_2	73.30
Al_2O_3	15.00
Fe_2O_3	1.51
TiO_2	0.17
P_2O_5	0.01
CaO	0.82
MgO	0.05
K_2O	4.13
Na_2O	3.37
Total	100.38

FORMULA

$$\left.\begin{matrix}0.3842\ K_2O\\0.4768\ Na_2O\\0.1281\ CaO\\0.0109\ MgO\end{matrix}\right\}\left\{\begin{matrix}1.2861\ Al_2O_3\\0.0825\ Fe_2O_3\end{matrix}\right\}\left\{\begin{matrix}10.684\ SiO_2\\0.787\ H_2O\end{matrix}\right.$$

APPROXIMATE MINERAL CONSTITUTION

	Per cent
Orthoclase	24.96
Albite	29.19
Anorthite[1]	8.39
Quartz	28.83
Kaolinite	8.63

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[1] See foot-note reference p. 349, *This Jour.*

Mixtures Made For the large scale tests, eleven different compositions were made consisting of 800 to 1000 pounds each. The materials were weighed on platform scales in batches of 200 pounds and tempered in a six-foot wet pan. After enough clay had been tempered with sufficient water for dry press molding, the remainder was tempered for molding by the stiff mud method. About 200 bricks were made from each mixture. Fifty to sixty of these were formed in a two-mold power driven dry press, and the remainder formed in a water-lubricated side-cut die attached to a stiff-mud auger machine. This brick machine has a rated capacity of 4000 to 7500 building brick per hour. The bricks were cut on a hand cutter set to cut fire brick size, or about $^5/_{16}$ inch wider than for cutting standard face brick.

After a mix had been expressed, the auger machine was cleaned before the next mix was introduced. The "left overs" from cleaning the machine were thoroughly mixed together and tested for molding properties in a "two hole" conduit die.

After the bricks were formed, they were dried in the open air to a leather-hard condition, then wrapped in paper, packed in excelsior and hauled by automobile to Columbus, Ohio, where the drying was completed and the brick burned at the Bureau's Experiment Station. The first lot of brick made in the large scale tests consisted of five different mixtures, as shown in the following table:

	Kaolin		
No.	G-35	G-8	Aplite
A-60	40	..	60
A-50	50	..	50
A-40	60	..	40
B-60	..	40	60
B-50	..	50	50

Results All five compositions molded perfectly in both the dry press and stiff mud machines.

The stiff mud brick containing G-35 kaolin cracked some in drying. The cracking was considerably less in those containing 40% kaolin than those containing 60%. None of the brick containing G-8 kaolin cracked in drying.

The brick when bone dry were set in a round down draft gas fired kiln with a setting chamber of 39 inches diameter and 39 inches high. The brick were burned to cone 9 in $35^1/_2$ hours and the kiln cooled and brick removed 36 hours after the fires were shut off.

All brick containing kaolin G-35 showed small cracks which were evidently drying cracks not visible when the brick were set and which opened up in the burning. None of the brick containing G-8 cracked in the burning.

The brick appeared to be well vitrified and were light gray in color, those containing G-35 being considerably lighter. The shrinkage was very high as the brick came from the kiln with a decided "hollow face" or "dish."

In the following table are given the shrinkages of brick made from those mixtures which came from the kiln in a sound condition. These shrinkages as well as all others following are calculated on "die length" as basis:

LINEAR SHRINKAGES

	Drying, per cent	Burning, per cent	Total, per cent
B-60 (dry press)	0.00	8.70	8.70
B-60 (stiff mud)	2.94	8.33	11.27
B-50 (dry press)	0.00	7.73	7.73
B-50 (stiff mud)	2.94	7.84	10.78

The Addition of Salt

A second lot of brick were made of both kaolins with aplite and NaCl added to determine its influence upon shrinkage and overcoming cracking. The amount of NaCl which was added dry to the charge in the wet pan was a little less than two-tenths of one per cent. The compositions of these two mixtures were as follows:

	KAOLIN			
No.	G-35	G-8	Aplite	NaCl
A-55	45 lbs.	....	55 lbs.	3 oz.
B-55	....	45 lbs.	55 lbs.	3 oz.

Both mixtures worked perfectly in both the dry press and stiff mud machines. Several lengths of two hole conduits were expressed without showing signs of cracking or tearing.

All pieces dried safely, and showed that the salt had overcome the cracking entirely, but appeared to have no appreciable effect on reducing the drying shrinkage. A thin "greenish yellow" scum with a salty taste occurred on the surface.

The brick were burned to cone 9 in 52 hours and cooled in 36 hours. None of the stiff mud brick of either mixture were cracked. The dry press brick of B-55 were also sound while about 10% of the A-55 dry press brick showed minor cracks. The scum which occurred during drying had formed brown stains on the dry press brick and a brown glaze on the stiff mud brick. The glaze was thicker, glossier and darker on brick containing G-8 kaolin than on those containing kaolin G-35. The brick were well vitrified and showed a high shrinkage. The total shrinkages are as follows:

TOTAL LINEAR SHRINKAGE

A-55, stiff mud.......	11.27%
B-55, stiff mud.......	11.76%
B-55, dry press.......	7.25%
A-55, dry press.......	(not determined)

The Addition of Sand

Quartz sand is instrumental in reducing shrinkage because of its volume changes. A mixture of 85% quartz sand and 15% ball clay will expand approximately $^1/_2$ inch in 12 inches when burned to cone 9. Therefore, burning shrinkage can be controlled within limits depending upon three factors:

1. Minimum clay content necessary for bonding strength and molding properties.
2. Minimum flux content necessary to control the degree of vitrification.
3. Maximum sand content permissible without danger of "checking" or "cracking" during burning.

The next lot of brick were made from a mixture consisting of 35% kaolin (G-8), 52$^1/_2$% aplite and 12$^1/_2$% quartz sand. Part of the brick were made dry press and the remainder were molded in the auger machine. Even with such a low kaolin content, the column issued from both the brick and conduit dies as near perfect as one would desire, indicating the remarkable molding properties of the kaolins.

The dry press and part of the stiff mud brick were thoroughly dry when set but part of the stiff mud brick still contained some moisture after 24 hours' drying in a gas fired drier. No cracking occurred during drying. The brick were burned in 54 hours to cone 9 and cooled in 36 hours. No cracked brick resulted from the burning or the rapid cooling. The addition of sand reduced the shrinkage appreciably, inasmuch as the brick were three-sixteenths of an inch longer than those previously made without sand. The total shrinkage of the stiff mud brick was 9.76%, a reduction of 2% over brick to which no sand was added. The total shrinkage of the dry press brick was 6.28%, making a reduction in shrinkage of 1.97%. Brick which were bone dry when set were light gray in color while those which were damp when set were "pink-gray." There was some indication that this color may have been due partly to scumming.

Six of the dry press brick and twelve of the stiff mud brick in the leather hard condition were shipped to the Fisk & Company plant at Darlington, Pennsylvania, where they were dried and set in the top of a round down draft kiln fired with natural gas and burned to cone 10 in 6 days. The brick were well vitrified and light gray in color. The total shrinkage was 9.8%.

Increasing the Sand and Adding $BaCO_3$

In the final lot of brick made, the sand content was increased to 18%

and 2 oz. of $BaCO_3$ added to 100 lbs. of the mixture. Mixtures were made using both kaolins separately and also the two mixed in equal parts. The compositions were as follow:

No.	Kaolin G-35	G-8	Aplite	Sand	$BaCO_3$
A-18	38 lbs.	....	44 lbs.	18 lbs.	2 oz.
B-18	....	38 lbs.	44 lbs.	18 lbs.	2 oz.
AB-18	19 lbs.	19 lbs.	44 lbs.	18 lbs.	2 oz.

The foregoing work demonstrated that such mixtures worked successfully in both dry press and stiff mud processes, and inasmuch as the stiff mud process appeared to be satisfactory in every way for these kaolins, and is therefore preferable, no dry press brick were made from the above three mixtures.

All three mixtures worked perfectly in both the brick and conduit dies. No cracking was observed during drying. The brick were set bone dry and burned to cone $8^1/_2$ in 50 hours, and cooled in 40 hours. A few of the A-18 brick cracked slightly during burning though this was not serious. None of the B-18 or AB-18 brick were cracked. The A-18 brick were light cream-gray while the B-18 brick were a little darker in color. The brick from all three mixtures were lighter in color than those previously made during these experiments. Evidently the improvement in color was due partly to the lower burning temperature and partly to the influence of the barium carbonate. The structure of the brick appeared to be dense though not thoroughly vitrified. The linear shrinkages of the three compositions were as follows:

	Drying shrinkage, per cent	Burning shrinkage, per cent	Total shrinkage, per cent
A-18	2.10	5.74	7.84
B-18	2.39	5.45	7.84
AB-18	2.25	5.61	7.86

The addition of sand made no appreciable difference in the drying shrinkage but reduced the burning shrinkage materially. The burning shrinkage was nearly 4% less than that of brick made without sand.

Conclusions

The foregoing results indicate that light cream and light gray face brick can be made from Georgia kaolin, aplite and sand. These brick compare favorably with the best face brick made from the fire clays of the Freeport, Mercer and Kittanning formations.

These kaolins are so plastic that mixtures containing as low as 35% kaolin to 65% non-plastic material mold readily by the stiff mud process. The stiff mud process is entirely satisfactory for such mixtures and is therefore preferable to the dry press process.

The so-called "soft" kaolins are friable and have low dry strength and are susceptible to cracking in drying and burning.

The so-called "hard" kaolins are the most desirable for brick making purposes. They have good bonding power and dry strength and will dry and burn without cracking.

Cracking during drying and burning of the soft kaolins can be eliminated by the addition of salt. If too much salt is added, it causes an efflorescence, brings soluble iron salts to the surface which develop into a brown discoloration or even a glaze on burning. The cracking caused by the soft clay can be overcome best by the addition of hard clay as was demonstrated in mix No. AB-18, a case of the "strong supporting the weak."

It has been demonstrated that such brick can be burned safely to cone 8 to 9 in 36 to 54 hours in a test kiln holding 200 bricks.

Brick containing 50% or less of kaolin when set bone dry offer no serious water smoking problem. They contain no carbon, pyrite nor other oxidizable matter, therefore, have no oxidation period; hence the burning can be carried on rapidly.

It is safe to say that a down draft kiln of seventy to eighty thousand bricks can be burned practically and economically in 3 to $3^1/_2$ days and cooled in a like period of time.

Raw Materials Available

The area along the lower edge of the Piedmont Plateau containing aplite low in iron and high in fluxes is in close proximity to the vast deposits of kaolin and white sand along the northern border of the Coastal Plain. These raw materials available for the manufacture of high grade face brick are sufficient to support a very large industry indefinitely.

Quarrying, transportation and grinding of the aplite rock will, of course, add to the production cost. As compared to face brick made from fire clays obtained by underground mining, the added cost of the flux is compensated for by the lower cost of mining the kaolin and sand by steam shovel.

There are several known areas of from 100 to over 600 acres in extent, underlaid with kaolins from 15 feet to over 40 feet in thickness. The overburden is comparatively light.

Fuel costs are higher in the kaolin districts than in the fire-clay areas, but the extra fuel cost is overbalanced by cheaper labor and the shorter burning time permissible with the kaolin mixtures.

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THE PROBLEM OF HEAT ECONOMY IN THE CERAMIC INDUSTRY[1]

BY WILLI M. COHN[2]

Introduction

The ancient arts have recently been included in and elaborated by technical science. Scientific investigation of the several fields has begun at the same time. Such a development, by no means final, may also be observed in the field of ceramics.

Operations in former periods were exclusively such that each factory or small shop used its own secret and carefully guarded methods and processes. Present-day practices show a departure from this. To make possible any scientific findings in the field of ceramics, an extensive publicity of the methods of operation and experience of the individual concerns is absolutely necessary. Not until then can science react helpfully upon practical problems.

Investigation methods of chemical science especially those of the chemistry of silicates and of colloids, of physics and of physical chemistry have been applied for clarifying the manifold phenomena in the field of ceramics. A considerable advance has been made in scientific ceramic investigation. A comprehensive summary of the results obtained from such investigations has been given by Rieke.[3]

The Significance of Heat Economy for the Pottery Industry

The greatest consumption of heat in the ceramic industry occurs in firing the products.

A considerable number of kiln-constructions have been designed for obtaining the maximum utilization of heat. For the special solution of this and other problems dealing with Heat Economy, the German Ceramic Society has founded the Bureau of Heat Economy. Its objects, according to Reutlinger,[4] are to produce high grade wares with (1) the least possible percentage of waste, (2) suitable fuels, (3) the least fuel consumption and (4) a minimum period of firing. Accordingly the scope of the Heat Economy Bureau is primarily:

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[1] A Dissertation submitted to the "Technische Hochschule" of Berlin in partial fulfillment of the requirements for the degree of Doctor of Engineering. Approved: April 18, 1923. Examiners: Professor Dr. Rieke, Professor Dr. Ing. Kloss.

[2] Dipl. Eng., Berlin.

[3] R. Rieke, "Neuere Fortschritte auf dem Gebiet der keramischen Chemie," *Fortschr. d. Ch. Phys. usw.*, 6 (1912).

[4] E. Reutlinger, "Wärmewirtschaftliche Untersuchungen an Brennöfen," *Ber. d. deutsch. keramischen Gesell.*, **2**, 2 (1921).

EDITORIAL NOTE: Received October 15, 1923, in German text through courtesy of Dr. R. B. Sosman and translated by us for appearance in this *Journal*.

See Louis Navias, "Measurement of the Heat Absorbed and Evolved by Clays during Firing and Cooling," *Jour. Amer. Ceram. Soc.*, **6** [12], 1268 (1923). Dr. Cohn did not have opportunity to read the contribution by Dr. Navias.

(1) Detailed examination of the present working methods to discover existing defects.

(2) Devising means for improvement, and training of firing and operating personnel.

(3) Supervising of application and continuance in practice.

(4) Investigation of the science fundamentals which are basic to exact knowledge of the heat requirements in industrial ceramic firing.

Heat Requisite for Firing Ceramic Wares

The heat requisite for firing ceramic products and inducted into the kiln is utilized as follows: (1) One part is consumed in obtaining the necessary maturing temperature. The higher the maturing temperature the more heat is required. Efforts are being made to get the same results with a lower degree of temperature.

(2) In the case of the finer grades, the articles during firing are placed in saggers which must also be brought to this high temperature and therefore require a considerable expenditure of heat.

(3) Another portion of the inducted heat serves to furnish the heat requisite for the reactions which absorb heat during the firing. It is also decreased by the quantity of exothermal reactions which, of course, are not considerable.

(4) The remainder of inducted heat is used in warming the walls of the kiln, in obtaining a satisfactory draft and in covering the losses due to radiation and conduction.

With ceramic materials not only the temperature but also the time of reaction plays an important part, as has been shown by the investigations of Rieke.[1] In this case also the consumption of fuel is essentially affected.

To obtain the finished product from the unfired mass only a portion of the inducted heat is utilized. What this amounts to can only be determined from a heating chart, and only on the basis of such charts can we make any recommendations for improving present conditions. Some attempts at preparing heating charts have already been made; but as yet the most important basic data are lacking, *viz.*, *specific heat*, and the extent of *heat change*[2] occurring during the firing.

The investigation here submitted purposes to fill this gap. It aims to determine specific heat and heat changes for the materials employed in ceramics at the usual temperatures—in great part at very high temperatures—and thus to establish the lacking groundwork. We shall first discuss previous attempts at establishing these values.

[1] R. Rieke, "Brenndauer und Brenntemperatur in ihrer Wirkung auf die Konstitution und Mikrostruktur des Porzellans," *Ber. d. deutsch. Keram. Ges.*, **2,** 2 (1921).

[2] Editorial Note: Wärmetönung, a difficult word to translate. It is the general term covering *heat of reaction*, *heat of fusion*, *heat of inversion*, etc. Throughout this treatise the author's use of the word "Wärmetönung" has been translated as "heat change" which admittedly is not sufficiently comprehensive.

Previous Methods for Determining "Specific Heat" and "Heat Change"

Frankenheim Heating and Cooling Curves

The so-called Frankenheim heating and cooling curves were devised to ascertain the behavior of a solid body during firing. The material to be tested, contained in a crucible, was placed into an electric furnace. At stated intervals, as frequently as possible, the temperature of the mass was read. Thus was obtained a *curve of temperature as a function of time.*

By comparing the temperature-time curve for the substance with that for the empty furnace it is possible to draw conclusions as to the behavior of the mass during firing. If there is a falling off in the temperature of the substance as compared with the temperature of the furnace, then a heat consuming process is taking place within the mass itself. If, on the other hand, the temperature advances, the process is one in which heat is liberated.

This method of thermal analysis has been applied to the chemistry of silicates by Tammann[1] and by the Geophysical Laboratory at Washington.[2]

Heating and Cooling Curves for Silicate Reactions

With reversible reactions it is immaterial whether the heating or the cooling curves are made, for in each the degree of temperature and the time of the reaction coincide.

The irreversible processes, as with silicates, show an entirely different behavior. In making cooling curves for silicates, strong under-coolings occur which may mount up to 150°C. Cooling curves for the silicates are therefore not admissible. Jaeger,[3] on this point, states as follows:

> The method of cooling (measured as a function of time), and the fixing of specific temperatures by means of discontinuities in the curve due to heat changes, fails absolutely within most silicates because of the slowness in reaching a condition of equilibrium. In spite of the very marked undercoolings and retardation which usually occur, Tammann's method for determining the duration of heat effects continues to be employed in obtaining fusion diagrams, and scarcely is it even suspected that under such circumstances this process is senseless and absolutely inadmissible.

Then, too, with too rapid a rate of heating the temperatures at which the reactions are observed to occur are above the required minimum as has been shown by Doelter[4] and Meissner.[5]

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[1] G. Tammann, "Kristallisieren und Schmelzen," Leipzig: Barth (1903).

[2] A. L. Day, "Die Untersuchung von Silikaten," *Z. f. Elektroch.*, 17 (1911).

[3] F. M. Jaeger, "Eine Anleitung zur Ausführung exakter physiko-chemischer Messungen bei höheren Temperaturen," Groningen: J. B. Wolters (1913).

[4] Doelter, "Physikalisch-Chemische Mineralogie," Leipzig: Barth (1905).

[5] B. Meissner, "Studien über Schmelz- und Umwandlungserscheinungen," Diss. Göttingen (1920).

Simultaneous Heating with Reference Substance

Satoh[1] in his investigations of Japanese kaolin proceeded according to the differential method suggested by White[2] and developed by Dittler.[3] The substance to be studied was heated simultaneously with a reference substance of known behavior. Unfortunately he chose quartz sands as the reference body, and failed to observe that its transformations at 575° and 800° should have appeared on the curves and should have been considered.

Standardized Rate of Heating

Friedrich[4] on the basis of the temperature-time curve established a heating-rate curve in order to show more clearly the behavior of a substance during heating. With the aid of a specially constructed regulating rheostat he was able to control the heating of the furnace in such a way that the rate of heating was uniform throughout the process.

These investigations were designed to give exact temperature-time curves, character of heat effects occurring, and temperature at which the reactions occur. However, they give no information as to the magnitude of the heat changes.

Heat of Crystallization

Tammann's process[5] has already been referred to, and its inadequacy noted. Vogt[6] is still employing it; but Plato,[7] in order to avoid undercooling uses inoculation thus obtaining an agreement in the fusion and solidification points. From the values obtained he calculates specific heat and heat changes. Koenigsberger[8] would determine heat changes from an extrapolation of cooling-curves according to definite assumptions, a procedure which cannot be applied to the silicates.

Another method was employed by Roos.[9] He charted cooling-curves of two substances, one of which has a known fusion and reaction heat.

[1] S. Satoh, "A Study of the Heating and Cooling Curves of Japanese Kaolinite," *Jour. Amer. Ceram. Soc.*, **4** [3], 182 (1921).

[2] W. P. White, "The Thermoelement as a Precision Thermometer," *Phys. Rev.*, **31,** 2 (1910).

[3] Dittler, "Beitrag zur Thermochemie der Silikate," *Z. f. anorg. Ch.*, 69 (1911).

[4] K. Friedrich, "Über ein einfaches Verfahren zur ersten Orientierung beim Studium der thermischen Dissociation und der Konstitution leicht zerlegbarer Mineralien," *Zentralblatt f. Min. usw.* (1912).

[5] G. Tammann, *loc. cit;* K. Hüttner und G. Tammann, "Über die Schemlzpunkte und Umwandwandlungspunkte einiger Salze," *Z. f. anorg. Ch.*, 43 (1905).

[6] J. H. L. Vogt, "Die Silikatschmelzlösungen," Christiania (1903).

[7] W. Plato, "Erstarrungserscheinungen an anorganischen Salzen und Salzgemischen," *Z. f. physikal. Ch.*, 55 (1906), 58 (1907).

[8] J. Koenigsberger, "Einfache Methode zur Bestimmung von Wärmetönungen bei Silikaten usw.," *Zentralbl. f. Min. usw.* (1912).

[9] D. Roos, "Über die Schmelzwärme und die Bildungswärme von Metallverbindungen usw.," Diss. Gött. (1916), *Z. f. anorg. Ch.*, 94 (1917).

By comparing the two curves he determined the heat variations of the body to be investigated.

Evaluation of Temperature-Time Curves

For evaluating the temperature-time curves White[1] proposes that the heat inducted into the material in a small, experimental, electrical furnace is proportional to the difference in temperature between furnace and material (G) to the time of action (Z) as well as to a constant (K) which he designated as "heat flow factor" or "radiation factor." G and Z can be determined. K may be dependent upon G and may vary with temperature, although this variation may not be determinable by experiment. Consequently G had better be held constant.

Thermal Microscope

Other investigators worked with the thermal microscope first constructed by Doelter.[2] The material to be tested was placed in a small electric furnace. The transformation temperatures could then be determined optically from the behavior of the material. This method has been used chiefly in physico-chemical petrography. Investigations which are of interest in ceramics were conducted by Mellor and Holdcroft,[3] Dittler,[4] Mellor,[5] also by Nacken.[6] Boeke[7] made use of the thermal microscope even under high pressure.

Microscopic Study of Powders

Bowen[8] was one of the first who worked the method now generally employed for silicates. The test substance is brought to a definite temperature and kept at this for a period—in some cases for several days—then quenched or chilled and microscopically examined. By narrowing down the intervals it is possible to determine with exactness the point of fusion.

Calorimetric Methods

Akerman[9] and his followers determined the heat of fusion of several substances by calorimetric methods. The apparatus used was primitive and their calculations vitiated by errors, some of them being considerable.

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[1] W. P White, "Schmelzpunktsmethoden bei hohen temperaturen," dto.

[2] Doelter, *loc. cit.*

[3] Mellor and Holdcroft, "The Chemical Constitution of the Kaolinite Molecule," *Trans. Ceram. Soc.* (English), 13-14 (1910-11).

[4] Dittler, *loc. cit.*

[5] Mellor, "Glazes in the Glost Oven," *Trans. Ceram. Soc.* (Eng.), 1912-13.

[6] R. Nacken, "Bestimmung der Schmelztemperaturen von Silikaten auf optischen Wege," *Silikat Zts.* (1913).

[7] H. E. Boeke, "Die Schmelzerscheinungen und die umkehrbare Umwandlung des Calcium Carbonates," *Neues J. f. Min. usw.*, 1 (1912).

[8] Bowen, "Schmelzerscheinungen bei den Plagioklas-Feldspaten," *Z. f. anorg. Ch.*, 82 (1913).

[9] Akerman, "Über die zum Schmelzen verschiedener Hochofenschlacken erforderliche Wärmemenge," *Stahl u. Eisen* (1886).

Heat of Solution

Another indirect method for determining heat changes which heretofore had been used primarily for the determination of fusion heat is based on the application of the first law of thermodynamics to chemical reactions. According to this the change in the energy of a body is independent of the manner in which it occurs.

The fusion-heat of a body is determined by dissolving its crystalline form in a given solvent and measuring the "heat of solution." The same body in a melted or amorphous (under-cooled) state is then dissolved in the same solvent and its heat of solution is established. Subtracting the two solution-heat values gives the heat of fusion or crystallization. In an analogous manner the other heat changes are determined.

Le Chatelier (summarized)[1] made use of this method and, after him, a whole series of investigators, one of them being Mixter.[2] It was applied by Mulert[3] to the chemistry of silicates especially quartz and several metallic silicates. The great difficulty, however, was in finding a suitable solvent for the silicates. He made use of a 20% hydrofluoric acid by which quartz and the metallic silicates could be dissolved within a period of 20 minutes. If the time necessary for dissolving is too long, the heat of solution in the calorimeter cannot be determined with necessary accuracy because of the rapid equalization of temperature between the calorimeter and its environment. Mulert even had some difficulty in dissolving pure alumina. With the double silicates of alumina he was able to calculate the requisite values, but he was unable to dissolve kaolin in sufficiently short time. Another large series of experiments was made by Heinrich.[4] He attempted to dissolve silica in hydrofluoric acid; but he was unable to secure complete solution.

The writer also first intended to determine the heat changes of ceramic materials according to Mulert's process. Numerous experiments were made with hydrofluoric acid of various concentrations; also with a mixture of hydrofluoric, hydrochloric and sulphuric acids in varying concentrations and proportions. An attempt was also made to bring about solution by heating the solvent. All these attempts, however, showed the impossibility of finding a suitable solvent in which fired porcelain, and the like, could be dissolved. With Portland cement matters are quite different.

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[1] Le Chatelier, "La silice et les silicates," Paris: Herman (1914).

[2] Mixter, "Bildungswärme und Polymerisation einiger Oxyde," *Z. f. anorg. Ch.*, 92 (1915).

[3] O. Mulert, "Über die Thermochemie der Kieselsäure und der Silikate," Diss. Göttingen (1912).

[4] K. Heinrich, "Über die in Flusssäure lösliche Modifikation des Siliciums," Diss. München T. H. (1919).

Nacken[1] succeeded in dissolving the cement by a mixture of hydrochloric and hydrofluoric acids. Thus he furnished the basis, up to then lacking, for the study of cement firing.

We have shown that with none of the previously used processes was it possible to determine experimentally the heat changes that occur during the firing of ceramic materials.

Specific Heat

Quite a number of processes for determining specific heat have been worked out. Tabulations can be found in Kohlrausch,[2] Burgess and Le Chatelier,[3] Stähler[4] and in many other places. The substance heated to a certain temperature, falls into a calorimetric vessel which has been filled with a liquid or is composed of a good heat conductor. The rise in temperature in the calorimeter is read, and the specific heat calculated for that definite temperature of the specimen. In this manner, taking point after point, it is possible to determine the change in specific heat. According to the investigations of Nernst and his collaborators[5] the specific heat of solid bodies near the absolute zero point is zero; it increases with temperature; the maximum value of the product of the atomic weight and of specific heat is about 6.4. According to the experiments of Richarz[6] and others, specific heat in the neighborhood of the fusion point assumes abnormally high values; this being caused by the fact that in these values, to a great extent, the fusion heat is included.

With silicates, and especially with ceramic materials, only a small number of investigations have been made. A method has been developed for silicates by White.[7] He employs an electric furnace placed directly above the calorimeter. After the test specimen has reached a definite temperature, it is dropped into the water of the calorimeter. In a similar manner Heyn, Bauer and Wetzel[8] examined a large number of fired fire-clay materials at temperatures as high as 1200°C.

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[1] R. Nacken, "Thermo-chemische Untersuchungen am Zementrohmehl und am Zement," *Zement* (1922).

[2] F. Kohlrausch, "Lehrbuch der praktischen Physik," Leipzig: Teubner (1910).

[3] Burgess and Le Chatelier, "Die Messung hoher Temperaturen," Berlin: Springer (1913).

[4] A. Stähler, "Handbuch der Arbeitsmethoden der anorganischen Chemie," 3, 1; Leipzig: Veit (1913).

[5] W. Nernst, "Die theoretischen und experimentellen Grundlagen des neuen Wärmesatzes," Halle: Knapp (1918); "Theoretische Chemie," Stuttgart, Enke (1921).

[6] F. Richarz, "Die Theorie des Gesetzes von Dulong und Petit," *Z. anorg. Ch.*, **59,** 59 (1908).

[7] W. P. White, "Specific Heats of Silicates and Platinum," *Amer. Jour. Sci.*, 28 (1909).

[8] E. Heyn, O. Bauer, E. Wetzel, "Untersuchungen über die Wärmeleitfähigkeit feuerfester Baustoffe," *Mitteil. aus. Königl. Materialprüfungsamt*, 2-3 (1914).

Other experiments were made with the copper calorimeter suggested by Nernst;[1] *e.g.*, the experiments of Magnus,[2] Drägert[3] and Steger.[4] These investigations, however, were confined to a few temperatures only. They give, therefore, but an incomplete picture of the behavior of ceramic materials during firing.

An examination of the specific heat of ceramic materials used in factories under all requisite temperatures is still lacking. Such a determination made by the method of mixtures cited above, with the aid of calorimetric experiments would require an immense amount of time and labor.

The impossibility of determining the heat changes as well as the difficulties in determining specific heat, have led the author to seek a process which makes possible a simple determination of the values referred to, and he believes he has found it in the process here to be described.

The Theory for a New Process for Directly Determining Specific Heat and Heat Changes

In order to determine specific heat (as well as the heat changes) directly in a given material, the temperature-heat-energy curve of this material must be known.

This curve, dependent upon temperature *t*, indicates what amount of heat is inducted into the weight-unit of the material. In the following, 1 gram (*g*) is taken as a unit of weight, and the quantity of heat is measured in small calories (cal); the quantity of heat inducted into the unit of weight is designated *q* and is measured cal/*g*. The determination of the values to be established proceeds as follows:

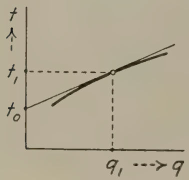

FIG. 1.

1. Specific Heat

In order to determine the true specific heat at a given temperature t_1 from the temperature-heat curve the tangent is drawn at the point in question in this curve (Fig. 1). The following equation then holds for the true specific heat C_w

$$C_w = \frac{q_1}{t_1 - t_0}$$

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[1] W. Nernst, *loc. cit.*

[2] A. Magnus, "Über die Bestimmung spezifischer Wärmen," *Ann. d. Phys.*, 31 (1910), *Phys. Zeits.*, 14 (1913).

[3] W. Drägert, "Thermodynamische Untersuchungen am Calciumhydroxyd, sowie über die graphische und mechanische Berechnung chemischer Affinitäten aus thermischen Messungen," Diss. Berlin U. (1914).

[4] W. Steger, "Über die mittlere spezifische Wärme einiger keramischer Massen in zwei verschiedenen Temperaturbereichen; Über die spezifische Wärme feuerfester Erzeugnisse," *Sil.-Z.*, **2** (1914).

2. Heat Changes

The heat changes occurring, which are conditional upon the transformations within the mass itself, show on the q-t curve. If the reaction takes place with great rapidity, the heat-absorbing reactions show as portions of the curve parallel to the q-axis. (Fig. 2.) Those reactions in which heat is set free appear as breaks in the otherwise even q-t curve. (Figs. 2 and 3.) In Fig. 2 the length of a-b gives directly the value of the heat absorbing reaction.

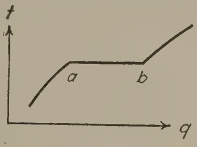

FIG. 2.

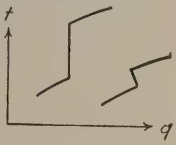

FIG. 3.

Determination of Inducted Heat

The difficulty now lies in determining experimentally the inducted heat, as requisite for the establishing of the q-t curves. This difficulty has already been pointed out by Jaeger[1] and White.[2]

Given the test substance S in a crucible T placed in an electric furnace O (Fig. 4) whose temperature is to be measured with the aid of thermoelement E. Let the thermoelement be placed exactly in the middle axis of the crucible halfway down into the substance. The heat, which is produced continuously in the furnace walls is transferred to the crucible through the air in the furnace, then penetrates the wall of the crucible and is conducted through the test-material to the junction points of the thermoelement. The quantity of heat inducted into the test material is then dependent upon:

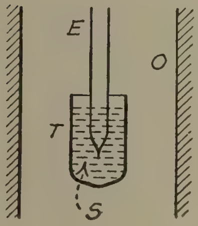

FIG. 4.

1. The degree of temperature prevailing in the furnace
2. The amount of heat transference by the layer of air in the furnace between the furnace wall and the crucible
3. The amount of heat penetration of the crucible material
4. The heat conductivity of the test material
5. The duration of the induction of heat.

Heat Conductivity of Test Material

The heat conductivity of the test material depends upon the kind of substance but varies within a narrow range at stated temperatures with ceramic materials. The earliest investigations for determining it were made by Paalhorn[3] and Hecht.[4] The materials specifically used in ceramics were treated by Nusselt,[1] Rinsum,[2] Goerens,[3] Knoblauch, Raisch and Reiher,[4] and other investigators. These investigators worked mostly at low temperatures; but Wologdine[5] worked with a considerably higher temperature and showed that the heat conductivity of all materials investigated by him hovers around a common median value. Also the very extensive tests by Heyn, Bauer and Wetzel[6] show that the conductivity of heat of similarly constituted materials at the same temperature does not vary much.

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[1] F. M. Jaeger, *loc. cit.*

[2] W. P. White, "Schmelzpunktsbestimmungen," *Z. f. anorg. Ch.*, 69 (1911); *Amer. Jour. Sci.*, 28 (1909).

[3] O. Paalhorn, "Über die Wärmeleitung verschieden zusammengesetzter Gläser," Diss. Jena (1894).

[4] H. Hecht, F. E. Neumanns, "Methode zur Bestimmung der Wärmeleitfähigkeit schlecht leitender Körper in Kugel- und Würfelform," Ph. Diss. Königsberg (1903).

Wetzel shows the increase of heat conductivity with increasing temperature, and this occurs in a similar manner in all materials. The results of these investigations are summarized in the "Sprechsaalkalendar."[7]

Simonis[8] is of the opinion that the conductivity ascertained for ceramic materials of varying composition but of similar porosity does not represent the conductivity of the materials but of the air contained within them.

Furnace Characteristic

It is thus possible to refer all the values requisite for the determination of heat q inducted into the material to:

1. The degree of the prevailing temperature, t
2. The amount of difference in temperature between furnace walls and crucible, G
3. The duration of induction of heat z, the relations being:

$$q = f(t,G,z).$$

The quantity of heat inducted into the crucible per unit of time is:

$$\frac{dq}{dz} = f_1(t,G)$$

dq/dz is thus dependent only upon t and G. If this function has once been established for a particular furnace then it holds good under absolutely similar test conditions *for all materials* of similar composition and heat conductivity. This could then be designated as the "furnace characteristic."

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[1] W. Nusselt, "Die Wärmeleitfähigkeit von Wärmeisolierstoffen," Diss. München, T. H. (1908).

[2] W. van Rinsum, "Die Wärmeleitfähigkeit von feuerfesten Steinen bei hohen Temperaturen usw.," Diss. München, T. H. (1914).

[3] P. Goerens, "Über die Wärmeleitfähigkeit feuerfester Steine;" Ber über 34. Hauptvers. d. Ver. dtscher. Fabr. feuerfester Prod., Berlin, *Tonindustrieverlag* (1914).

[4] O. Knoblauch, E. Raisch, H. Reiher, "Wärmeleitzahl für Bau- und Isolierstoffe usw.," *Gesundheitsingenieur,* 43 (1920); Ref. *Das Gas- und Wasserfach,* 64 (1921).

[5] Wologdine, "Untersuchungen über die Wärmeleitfähigkeit, Porosität, und Gasdurchlässigkeit der feuerfesten Materialen," *Sprechsaal,* 1909.

[6] Heyn, Bauer and Wetzel, *loc. cit.*

[7] "Sprechsaalkalender," Coburg: Müller & Schmidt (1922).

[8] M. Simonis, "Beitrag zur Bestimmung der Wärmeleitfähigkeit von Chamotte Ziegeln, etc.," *Sprechsaal* (1908).

Determination of Furnace Characteristic

For the purpose of determining the *characteristic of a furnace* the knowledge of q is essential for some given material; q depends upon temperature as does the true specific heat c_w. Both values are related as follows:

$$dq = c_w . dt$$

If, then, by any process c_w has been established for a given substance in relation to temperature, then q (expressed in cal/g) can be calculated.

If, by experiment, a temperature time (t-z) curve is established for the same material for which q has been determined, then the two curves may be converted into one. We then obtain from the q-t and the t-z curves a q-z curve. By differentiation of this curve a dq/dz curve can be established in its dependence upon z or t, respectively. Should G be considered constant during the experiment then the last-named curve holds only for this one definite G. Thus we have met the conditions and have found for the furnace in question:

$$\frac{dq}{dz} = f_1 (t,G)$$

A similar curve may also be made for another G, enabling us to finally obtain a curve chart of the furnace characteristic, from which dq/dz may be read for any temperature or temperature gradients in furnace walls and crucible.

To establish a temperature-heat-energy curve for any kind of material which falls under the aforementioned conditions, from which the specific heat and heat changes must result indirectly, it is necessary to construct the curves for temperature and temperature differences, dependent upon time, for such material according to the established test-conditions. From this we establish the dq/dz curve with the aid of the furnace characteristic. By integration we find the q-z and then the desired q-t curve.

Summary

The steps for determining the unknown quantities which are necessary for the study of heat economy are:

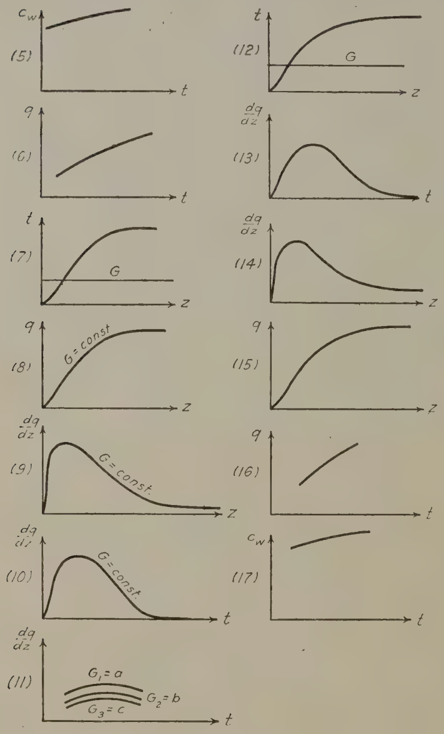
A. Calorimeter tests for the determining of q.
   1. Determining specific heat as a function of temperature (experiment) c_w-t curve (Fig. 5).
   2. Calculations of the inducted heat as a function of temperature; q-t curve (Fig. 6).

B. Determining the furnace characteristics on the basis of the same material as used for "A."
   1. Making a temperature-time curve with constant temperature gradients between furnace-wall and crucible. (Experiment): t-z curve (Fig. 7).

2. Determining the q-z curve for a constant G (graphically) (Fig. 8).
3. Differentiation of the q-z curve (Interpolation calculation after Thiele[1] and Sanden[2] $\frac{dq}{dz}$-z curve) (Fig. 9).
4. Determining the $\frac{dq}{dz}$-t curve with a constant G (graphically) (Fig. 10).
5. Making a curve chart by determining corresponding curves for a varying G (Fig. 11).

C. Determining the q-t curves of various materials.

1. Making t-z curves for various substances with a constant G (Fig. 12).
2. Determining the $\frac{dq}{dz}$-t curves from the curve charts (Fig. 13).
3. Determining the $\frac{dq}{dz}$-z curves (Fig. 14).
4. Graphic integration for determining the q-z curves (Fig. 15.)
5. Making the q-t curve for the material in question (Fig. 16.)



FIGS. 5–17.

Furnace Characteristics Determined from t-z Curves

The finding of furnace characteristics can also be done in a somewhat different manner. During the investigations it has appeared that it is generally impossible to control the heating of the furnace sufficiently to keep the temperature gradient between furnace wall and crucible constant at a given temperature. Theoretically, also, it does not seem possible to have G constant during the experiment as has been shown by White.[3] The making of a curve chart was therefore attempted on the following considerations:

The same curve chart, "furnace characteristics," will also be obtained if G is known for every point of the t-z curve, as well as for the curves developed therefrom. Consequently, if for the same substance several $\frac{dq}{dz}$-t curves have been determined, and points with a coinciding G are joined, we obtain the same curve chart as above (Fig. 18).

If in these experiments more than 1 g. of the substance is used—as is here assumed—it will have to be considered for the furnace characteristic.

[1] T. N. Thiele, "Interpolationsrechnung," Leipzig: Teubner (1909).

[2] H. v. Sanden, "Praktische Mathematik," Berlin: Urban (1920).

[3] *Loc. cit.*

D. Determining the specific heat for the various temperatures (according to Fig. 1) for the test material (Fig. 17).

E. Determining the extent of the occurring heat changes (according to Figs. 2 and 3).

Experimental Arrangements for Determining the *t-z* and *G-z* Curves

The making of the temperature-time and temperature-difference time curves was done in the following manner:

The Furnace

A tubular resistance furnace with outside platinum foil winding[1] furnished by the Heraeus Company, was set up vertically. Its capacity was 14 amp.; 220 volts.

Maintenance of Zone of Uniform Temperature

The main difficulty with such types of furnace consists in obtaining and maintaining a zone of uniform temperature,[2] particularly with low temperatures. According to Ostwald-Luther[6] the most advantageous type of vertical furnace is one in which the furnace is completely closed at the top and where the removable cover is placed at the bottom.[7] By this arrangement air currents are almost entirely eliminated.

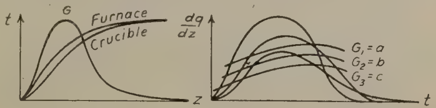


FIG. 18.

In order to obtain the maximum of temperature constancy the tubular furnace was closed below by several asbestos and fire-clay plates. On top was placed a close-fitting cover of fire clay in which were left the necessary openings for the protection tubes of the thermoelement, thereby shutting out the current of air except for the minimum that would enter through the cracks. It was actually shown that the zone of constant temperature remained almost always at the same point. The construction of the furnace is shown in Fig. 19.

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[1] According to Bronn such types of furnace are quicker in action than those wound with platinum wire. Bronn, "Der elektrische Ofen im Dienste der keramischen Gewerke," Halle Knappe (1910).

[2] See Lucas;[3] Jaeger;[4] White.[5]

[3] Lucas, "Feuerschwindung," Diss. Göttingen (1903).

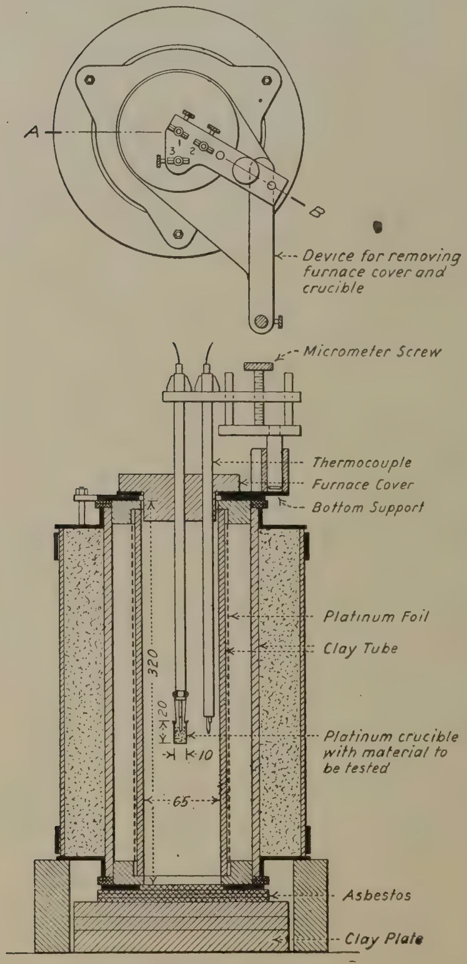
[4] F. M. Jaeger, *loc. cit.*

[5] W. P. White, *loc. cit.*

[6] Ostwald-Luther, "Physiko-chemische Messungen," Leipzig: Engelmann (1910).

[7] Lucas, Jaeger and White did their work in furnaces some of which were open from below and others but imperfectly closed. Naturally there arises a strong convection current making it difficult to obtain a zone of equal temperature. According to Ferguson (J. B. Ferguson "Temperature Uniformity in an Electric Furnace," *Phys. Rev.*, 12 (1918)) a perfectly uniform distribution of temperature can only be obtained in horizontal furnaces both ends of which are alike heated.

Maintenance of Temperature The processes to be investigated require a maximum temperature of 1400°C which was easily obtained even though the winding was on the outside. The furnace was heated by a 220-volt direct current regulated exactly by resistance. The connections are indicated in Fig. 20. The apparatus was so arranged that the readings of an ammeter, as well as the regulating were easily accomplished from a sitting position.



Section at line A-B

Fig. 19.

The Crucible The test material was placed in a small crucible of iridium-free platinum, furnished by Heraeus. This crucible had the shape of a cylinder 10 mm. in diameter, 20 mm. in length, closed at the bottom. *Its capacity was about 2 g.*[1]

At the upper end of the crucible were three holes about 1 mm. in diameter 120° apart for the purpose of suspending the crucible. The crucible was filled almost up to the holes.

In order to avoid a loss of heat the crucible was not supported from below in the furnace but suspended on the thermoelement protection tube. (Cf. Fig. 19*a*.) In this manner, above all, we avoided having an opening in the bottom of the furnace.[2] By this arrangement it was possible to control absolutely the insertion of the thermoelement. It is of chief import to measure the temperature exactly at the medial axis of the platinum cylinder and exactly at half the height of the material. With this experimental apparatus[1] it is possible to actually observe the insertion of the thermoelement into the finely powdered mass.

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[1] This arrangement, like those of White, *loc. cit.* and Jaeger, *loc. cit.* purposes to minimize as much as possible the temperature difference between the center of the crucible and the crucible wall, as well as to exclude as much as possible the influence of variations in heat-conductivity of the test material.

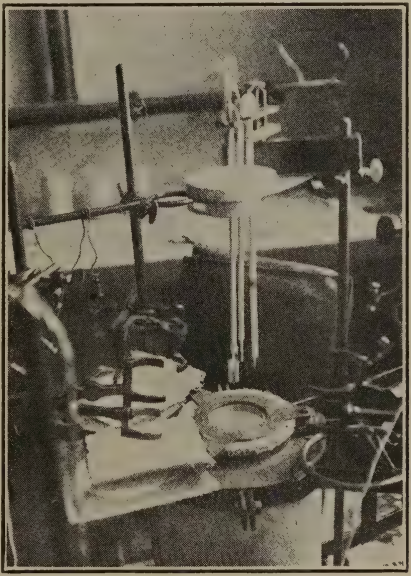
[2] Contrast with Jaeger, who accomplished the suspension by cylindrical platinum sheets as connecting links between the protection tube and the crucible.

Thermocouple The thermocouples used were platinum-platinum 10% rhodium, by Heraeus, of 0.4 mm. thickness.

According to Day and Sosman[2] such thermoelements at 1200° show a variation of ±1°C; at 1600° ±1.5°C. These measurements were generally made with the junction points unprotected.[3]

In order to secure a more sensitive measurement the temperature difference between furnace and crucible was determined directly according to the differential method by juxtaposition of two thermoelements. Moreover, it was requisite to measure the degree of heat prevailing at any moment of time. We accomplished this by placing a third thermoelement into the furnace.

The two thermoelements for measuring the furnace temperature were equidistant from the center of the furnace; they were sufficiently distant one from the other so as not to interfere with each other in their registration.[4]



Before the experiment.
FIG. 19*a*.

The junction points of each thermoelement extended about 7 mm.

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[1] In consequence of the prevailing shortage of platinum it was not possible to construct a Faraday screen, so as to avoid disturbances in the thermoelement under extreme heat which causes ionization of the air. Disturbances of this sort, according to Jaeger, *loc. cit.* occur only at temperatures higher than 1400°, and chiefly in furnaces with inner coils. The limits of temperature of the measurements made by us generally were lower than that, so that an error can scarcely have occurred within this range.

[2] A. L. Day, R. B. Sosman, E. T. Allen, "High Temperature Gas Thermometry," *Carnegie Institution Publication*, 157 (1911).

[3] To determine the temperature gradient G between the furnace wall and crucible two thermocouples are necessary. See Bronn, *loc. cit.*, White, *loc. cit.*, Jaeger, *loc. cit.*

[4] In consequence of the individual conductivity of heat in each thermoelement it might otherwise have occasioned a lowering of temperature within its immediate environment; this would have disturbed the indications of the other element.

The three thermoelements were placed to form approximately an equilateral tribeyond the protection tube. To obtain an exactly parallel and permanently fixed position of the thermoelements they were carried over a considerable length by the cover. Above the cover was a contrivance which, by means of a micrometer screw, made possible from above a fine adjustment of the three thermoelements. It served the purpose of determining exactly the location of the zone of constant temperature and to adjust the thermoelements accordingly. The protection tubes at their upper ends had an offset which absolutely prevented their slipping down into the interior of the furnace. (Cf. Fig. 19.)

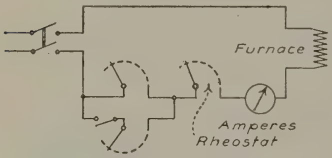

Fig. 20.

A special device which may also be observed in Fig. 19, made it possible to withdraw completely from the furnace both the cover, the thermoelements and the platinum crucible as well as to swing them aside so that the adjustment of the thermoelements and also their centering in the mass, etc., could be accomplished *outside* of the furnace. The whole could then again be lowered into the furnace. The free terminals of the thermoelements were placed in melting ice which was kept in double-walled vessels. The thermoelement serving for measuring the temperature of the furnace was connected directly through a moving-coil galvanometer.[1]

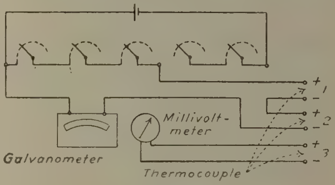

Fig. 21.

The two thermoelements in differential position were connected through a compensating device.[2]

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angle (in outline), its one corner being in the axis of the furnace. The exposed junction points of each element were on exactly the same level in the furnace.

This arrangement, when compared with that of Austen, and employed by Dittler, *loc. cit.* (2 thermoelements in the crucible, one outside of it) has the advantage that the thermoelements do not dissipate too much heat from the mass.

Furthermore, it is preferable to employ as reference temperature, the temperature of the furnace, which is always changing in the same way under similar test conditions, inasmuch as the crucible temperature constantly changes because of the reactions occurring during heating.

[1] Type Deprez-d'Arsonval (make: Keiser & Schmidt), sensitivity 10^{-4} amp.

[2] Type Poggendorff as indicated by Kohlrausch connected with a zero instrument (make: Siemens & Halske), sensitivity 3.10^{-7} amp. The connections can be seen in Fig. 21. The storage cell of the compensator was calibrated daily by comparing it with a normal element; compensation was made in the usual manner. The different temperatures were read by means of calibration curves in millivolts. The investigations with the compensation apparatus were made according to the detailed directions of Jaeger, *loc. cit.* On account of the limited funds available it was impossible to provide a Diesselhorst potentiometer, free from thermo-e.m.f.

Determining the *t-z* and *G-z* Curves

The Sample In order to obtain measurements that are actually reproducible, the material must always have the same granularity as well as be of the same average composition.[1]

The materials were pulverized in large quantities and ground for eight hours in the porcelain mill. They were then put through a very fine lawn. The rest of the soft materials, such as kaolins and clays, were examined in the slimed state.

Operating the Apparatus The test material was dried for two hours at 125°. Two grams were weighed out and placed in the platinum crucible. By proper shaking it was possible to so put the mass into the crucible that it always reached the same level—usually close to the holes made for suspending the crucible.

The crucible was then suspended—outside of the furnace—the thermoelement carefully inserted to proper depth exactly in the center of the crucible, then the whole was swung over the furnace and gradually lowered. The two other thermoelements had previously been carefully adjusted.

Preliminary Tests

The preliminary tests were to find the zone of constant temperature in the furnace. The furnace was kept at constant temperature for a considerable time. The thermoelements were raised and lowered and then by accurate adjustment with the micrometer-screw the desired region having a range of 45 mm. was determined. By several similar tests, under different temperatures, we checked up the location of this zone. Even during the tests frequent checks were made. From these it appears that this zone varied only within a few millimeters.

Rate of Heating Wohlin[2] in making heating curves proceeded by gradually increasing the current which he used for heating the furnace. He increased the current every five minutes by $^1/_2$ amp. The curve resulting appears as a uniform slowly rising line. But when a curve of similar sort was made with our more exact testing device, it appeared that for each increase in the heat current there was a corresponding irregularity in the heating curve. This can be seen in Fig. 22. The upper curve shows the temperature of the furnace, the next lower that of the crucible; the lowest curve on a scale five times enlarged, shows the difference in the temperature of both—(G-z curve). If, on the other hand, the furnace temperature was but gradually increased the smaller heat effects were almost unobservable.

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[1] Leitmeier, "Zur Kenntnis der Schmelzpunkte von Silikaten," *Z. f. anorg. Ch.*, 81 (1913), proposes that test material be finely pulverized in an agate mortar, slimed and the suspended part only be used. Such a process, of course, is exceedingly troublesome and time consuming; moreover it is probably not wholly free from objections since the particles of greater specific gravity settle on the bottom and thus escape examination (*e. g.*, quartz particles, etc.).

[2] R. Wohlin, "Beiträge zur thermischen Analyse von Tonen, Bauxiten und einigen verwandten Körpern," Diss. Breslau (1913).

It had been stated that it was exceedingly difficult to conduct the heating so that G would remain absolutely constant during a test. It has also been known that this does not seem desirable, even from a theoretical point of view. The irregularities occurring from this could only be ascertained by means of the differential method.

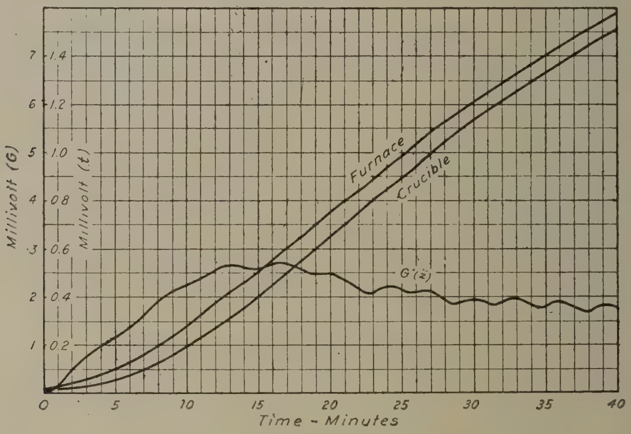

FIG. 22.

The numerous curves necessary for obtaining the curve chart dq/dz-$(t_1.G)$ were obtained as follows: In one experiment a definite current of 14 amperes was switched on and the curve resulting was made without further regulation of the current. In another experiment a definite current was continued by *constant* regulation during the entire process. In both cases there resulted quite uniform curves, rising in the beginning, but subsequently declining gradually. With an energy supply constantly kept at 14 amp. and 220 volts (= 3080 watts) a temperature of about 1400°C could easily be obtained in about 90 minutes.

Readings were taken every ten seconds; alternately reading furnace temperature and temperature differences. Time was indicated by a clock striking every ten seconds.

(*To be continued*)

NOTE ON AN UNUSUAL CASE OF WARPING OF FLAT WARE IN THE GLOST KILN[1]

By Thomas A. Shegog

ABSTRACT

The warping of flat ware in the glost kiln can apparently be caused by the "pull" of a cooling glaze, provided the glaze solidifies before the body has become entirely rigid.

Seven-inch plates of the regular biscuit ware which had been fired to cone 8 half over, and which had an absorption of 7.5 to 9%, were dipped in a trial glaze by the regular dipper and fired for 22 hours in the second ring of the glost kiln. One bung of plates with this glaze was placed in a sagger and the saggers placed 5, 8, and 13 high, respectively. A second bung in each sagger was similar ware dipped in the regular glaze. The trial glaze was as follows:

Frit		Mill Batch	
Borax	23.5	Frit	40.25
Whiting	18.5	Flint	10.50
Flint	30.5	Cornwall Stone	28.75
Soda Ash	12.75	White Lead	21.00
China Clay	14.75		
	100.00		100.50

Taking Cornwall Stone as equivalent to:

China Clay	34
Feldspar	31
Quartz	35
	100

the molecular formula of the glaze is:

$$\left.\begin{array}{l} 0.340\ Na_2O \\ 0.051\ K_2O \\ 0.346\ CaO \\ 0.262\ PbO \end{array}\right. \quad 0.280\ Al_2O_3 \quad \left.\begin{array}{l} 2.822\ SiO_2 \\ 0.230\ B_2O_3 \end{array}\right.$$

Oxygen ratio 3.44

$SiO_2 : B_2O_3 :: 1 : 0.0815$

Veritas firing rings were placed in each sagger and they measured 19½, 20 and 21, reading from the bottom upwards.

The second bung of plates in each sagger (dipped in the regular glaze) was perfectly straight, as was also the ware throughout the rest of the kiln, but those in the three bungs which had been dipped in the trial glaze were warped to a surprising extent. This glaze had not matured.

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[1] Presented at Atlantic City Meeting, Feb., 1924 (Whitewares Division).

Several weeks later, the experiment was repeated under precisely the same conditions, but the glost fire was a little harder. The glaze was consequently better matured though still underfired. The result was that the plates came out much straighter, though still more or less warped.

The warping is manifestly caused by the glaze since that is the only variable. I have tried to explain it to myself by assuming that the body softens slightly in the glost fire, and that when the kiln begins to cool, the glaze solidifies before the body has become entirely rigid, and that during solidification the contraction of the glaze is sufficient to pull the still soft body out of shape.

The smaller degree of warping of the second series of trials might be accounted for on the assumption that as the glaze is nearer maturity it has reacted with the constituents of the body to a greater extent and so reduced the difference in contraction.

This explanation does not seem convincing and was only arrived at by a process of elimination. If it were true, one would expect that the glaze (especially in the first series of trials) would be more or less in a state of tension and hence very liable to craze. This, however, is not so. The glaze on the first series of trials, notwithstanding its immaturity, withstood five chillings from 200°C in water at 15°C on some of the plates, on others it crazed slightly on the foot at the fifth chilling.

In the second series of trials, the glaze though better matured, crazed more easily. Three plates were tested and each crazed on the foot on the second chilling from 200°C to 15°C. This seems inconsistent with the suggested explanation.

As I have failed to find any reference in the literature to such a case of warping, and have been unable to find anyone who has met with it or who can throw any light on the cause, I have brought it before the SOCIETY in the hope that some member may be able to suggest an explanation.

The resistance to crazing of the first series seems remarkable, not only because of the immaturity of the glaze but also because of its high soda content.

SEBRING POTTERY COMPANY
SEBRING, OHIO

NOTE ON THE RATIONAL ANALYSIS OF CLAYS[1]

By G. S. Tilley[2] and J. D. Sullivan[3]

ABSTRACT

Several feldspars, muscovite, biotite and quartz, as well as diaspore clay and kaolinite, in fairly pure state, were severally subjected to the procedure of "rational analysis" of clays. It was shown by analysis of the residues and solutions obtained:

1. That all the feldspars were attacked to a greater or less extent
2. That the micas were attacked more than the kaolinite
3. That kaolinite was not wholly decomposed by the treatment
4. That diaspore clay was not approximately decomposed by the treatment
5. That the amount of decomposition of all the substances depends to a considerable extent on the time and temperature of treatment.

As a result of these conclusions, it would not be possible to draw any conclusion as to the clay substance content of a particular clay from the results of a rational analysis.

As a further result, it would not be possible to draw any conclusion as to the content in feldspars and quartz by further analysis or treatment of the residue from acid treatment, because the feldspars would have already been dissolved out in part before the attempt was made to determine them by this procedure.

The method, whatever its empirical value, cannot be said to show even approximately either clay substance, feldspars, micas, or quartz in any given clay.

In connection with experimental work being carried on by the Bureau of Mines with the object of developing a process for preparing aluminum sulphate from clays, it has been desirable to know the approximate mineralogic composition of the clays used. The methods available were "rational analysis," microscopic examination, and calculation of the so-called "norm" from the chemical composition of the clay as determined by analysis.

On investigating the methods themselves, we found, as Washington says[4] that "there is great divergence of opinion, even among ceramists themselves as to the value of the 'rational' analysis."

It seemed to us that a study of the action of the procedure of the rational analysis on the pure minerals themselves, which occur as a mixture in clay might throw some light on the controversy. We, therefore, obtained in a quite pure state the following minerals:

Orthoclase
Albite
Oligoclase
Microcline
Labradorite
Quartz
Muscovite
Biotite
Kaolinite

All of them were ground to pass 100-mesh, and examined with the microscope by methods of *Bulletin* **679** of the U. S. Geological Survey, and found to have at most very slight admixture with foreign substances.

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[1] Published with permission of the Director, U. S. Bureau of Mines.

[2] Associate Chemist, Pacific Expt. Station, Bureau of Mines, Berkeley, California.

[3] Junior Physical Chemist, Pacific Expt. Station.

[4] *Jour. Amer. Ceram. Soc.*, **1**, 406 (1918).

A sample of diaspore containing 80% alumina was also obtained, ground and examined, and treated as were the other nine minerals. All ten were put through the process of rational analysis,[1] as far as determining the alumina dissolved by the acid treatment. Briefly, the method consists in heating the substance with sulphuric acid solution till fumes of sulphuric acid appear. Kaolin is expected to dissolve and micas and feldspars remain insoluble. Hence analysis of the soluble and insoluble portions is supposed to give figures which are functions of the content of the sample in kaolin and the more complex silicates. Our results were so significant that it was considered unnecessary to go on with the determination of the silica and alumina in the undissolved residues.

The results of the determination of iron and alumina in the solutions are tabulated in the following table:

Substance (1 g. each sample)	Analysis of solutions (total amount of each constituent found)		Substance (1 g. each sample)	Analysis of solutions (total amount of each constituent found)	
	Alumina	Ferric oxide		Alumina	Ferric oxide
Biotite	0.1260	0.1660	Albite	0.0008	0.0009
	0.1192	0.1025		0.0024	0.0009
Muscovite	0.3433	0.0227	Quartz	0.0002	0.0009
	0.2911	0.0197		0.0004	0.0009
Orthoclase	0.0030	0.0005	Kaolinite	0.1819	0.0179
	0.0004	0.0009		0.1677	0.0203
Microcline	0.0034	0.0018	Diaspore	0.0190	0.0220
	0.0037	0.0028		0.2729	0.0370
Labradorite	0.0843	0.0072	Oligoclase	0.0027	0.0018
	0.0169	0.0063		0.0054	0.0028

In several tests the samples were evaporated to fumes more slowly than the others, with the result that in every case of slow evaporation the amount of alumina in the solution was considerably more than with the others, although both conformed to the directions for the analysis. This effect is most noticeable with diaspore and muscovite, but shows also with kaolinite and biotite. This is in agreement with numerous observations during our work here on the decomposition of clays by sulphuric acid. We found in practically every case in which the acid rapidly came to a condition of high concentration, that the action on the clay minerals was much less than when the acid contained water sufficient to dilute it to at most 70–75% H_2SO_4 for a longer time, other conditions being equal. We ascribed this to the formation of an insoluble protecting layer on the surface of the mineral grains, and found that such an insoluble acid aluminum sulphate did exist. It is easily made, for example, by adding concentrated sulphuric acid to a strong solution of aluminum sulphate, the resulting precipitate not being precipitated out simply by common ion effect, but being a compound of the composition $Al_2(SO_4)_3.H_2SO_4$. Analysis of the insoluble compound obtained by heating clays with sulphuric acid at higher temperatures appears to be more nearly $Al_2(SO_4)_3.2H_2SO_4$, by determination of the ratio of SO_4 to Al_2O_3.

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[1] U. S. Bureau of Mines, *Bull.* **53,** 38–41.

It is very slowly decomposed even by boiling water—cakes of decomposed clay cemented together by this substance often taking two days digestion on the steam bath to break up a cake weighing only 25 grams.

The formation of this insoluble substance under the conditions of the rational analysis, and directions for avoiding it, or dissolving it after formation must be taken into account by any method claiming accuracy.

Washington[1] mentions as factors seriously influencing the results, the concentration of the reagent, the time of treatment, temperature of treatment, and whether this is attained suddenly or gradually, or is uniform or varied during the treatment. These all bear on the formation of this insoluble acid sulphate of alumina whenever the acid becomes concentrated to about 75–80%, with consequent protection of the minerals from further action to greater or less degree.

In other words, it is almost impossible to obtain the same results on the same substance without the most careful regulation of the conditions of attack by sulphuric acid.

Further, a study of the table of results will indicate at a glance the impossibility of calculating "clay substance" from the percentage of alumina in the solution. The feldspars are all attacked to a greater or less amount, and the micas are attacked almost as much as the kaolinite itself. The fact that the feldspars are attacked and go into solution to a certain extent renders the determination of alumina and silica in the undissolved residue as a means of calculating feldspathic constituents worthless, the percentage error in that case being as much greater than in calculating clay substance by dissolved alumina as the clay substance exceeds the feldspathic constituents.

We are, therefore, inclined to agree with Washington[1] in deciding that "the methods of 'rational' analysis can furnish little but approximate and uncertain, and probably more or less erroneous and misleading, information."

The results with diaspore, even on the prolonged digestion resulting in the higher extraction of alumina, show that in the case of high alumina clays or "jehytes" of which diaspore is a type, the method of rational analysis completely fails to give even an approximation to the true content of clay substance.

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[1] *Loc. cit.*, p. 408.

THE OXIDATION OF CERAMIC WARES DURING FIRING[1]— II. THE DECOMPOSITION OF VARIOUS COMPOUNDS OF IRON AND SULPHUR UNDER SIMULATED KILN CONDITIONS[2]

By Frederick Gray Jackson[3]

Ferric Sulphate in Clay

So far we have got along without having to go much into balanced actions. The case of ferric sulphate, however, the final product formed in the weathering of iron-sulphur compounds in clays, calls for a consideration of a balanced action. It would seem that, particularly in an atmosphere of pure oxygen, the reaction

$$Fe_2(SO_4)_34H_2O = Fe_2O_3 + 3SO_3 + 4H_2O$$

would proceed without hindrance to completion. We must remember, however, that the reaction

$$2SO_2 + O_2 \rightleftarrows 2SO_3$$

is a balanced one, and that hot clay is a good catalyst. The equilibrium point of this reaction changes with changing temperature. With this in mind, it is not so surprising to find, beginning at about 500°, a marked evolution of SO_2. There is also the probability that some of this SO_2 recombines with iron oxide to form an incompletely oxidized compound or iron and sulphur. The possibilities are ferrous sulphate, basic sulphates, sulphites, and possibly hyposulphites. There may be several different compounds formed with various decomposition temperatures. The problem, therefore, becomes more complicated.

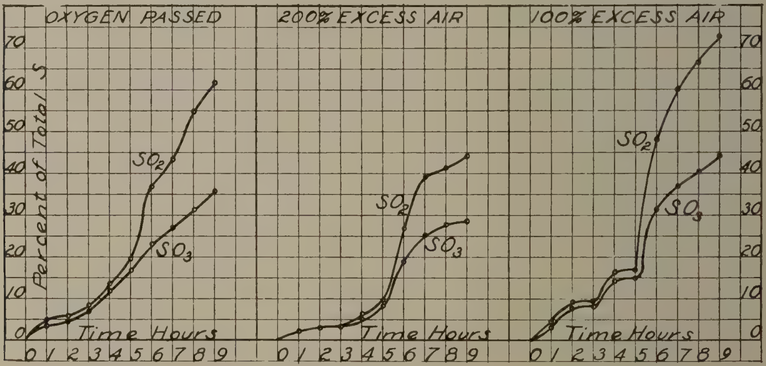

Fig. 7.—Ferric sulphate.

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[1] Published by permission of the Director of the U. S. Bureau of Mines.

[2] For Part I of this paper see *Jour. Amer. Ceram. Soc.*, **7** [4], 223 (1924).

[3] Associate Chemist, Ceramic Station, U. S. Bur. of Mines, Columbus, Ohio.

A further complication arises when we add CO_2 to the atmosphere. There is then the possibility of forming, not only the above compounds by reaction of iron oxide and water with SO_2, but also oxycarbonates as well as mixed compounds. Iron lends itself well to the formation of complex molecules, the nature of which is particularly difficult to discover. It will be noticed in both experiments where CO_2 is passed over ferric sulphate that there is a slackening of sulphur evolution during the third hour. It is probable that some secondary reaction took place at that time, which changed the whole course of the succeeding action.

When the amount of oxygen is still further reduced, we have a second pause in sulphur evolution during the fifth hour. This is evidence of further complicating actions. During the sixth hour, in all cases, there was a marked increase in evolution both of SO_3 and SO_2, but particularly so in the case under consideration. (See Fig. 7.) To get to the bottom of this subject might require years of experiments.

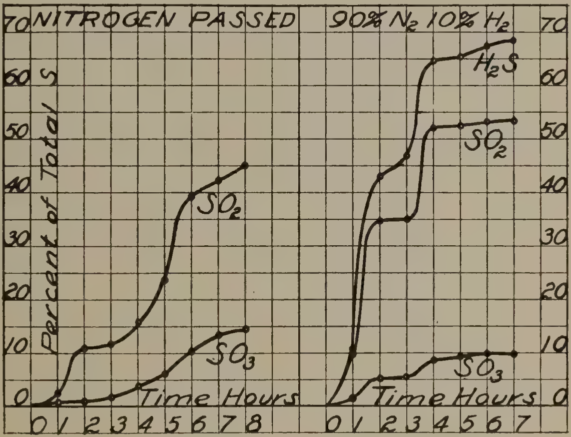

FIG. 8.—Ferric sulphate.

When ferric sulphate in clay is heated in an atmosphere of pure nitrogen, it would seem at first as if the reaction should proceed as

$$Fe_2(SO_4)_3 = Fe_2O_3 + SO_3$$

with no SO_2 formed. However, the reaction

$$2SO_3 \rightleftharpoons 2SO_2 + O_2$$

has an equilibrium point in the presence of a catalyst such as hot clay. The position of this equilibrium point, as well as the time in which it is reached, varies with the temperature. The tendency appears to be the formation of more SO_2 at low than at high temperatures. Since the rate of evolution of SO_3 varies with the temperature, the problem becomes very complicated. It was hoped that, in burns in an atmosphere of pure nitrogen, some calculation of the iron-sulphur-oxygen ratio remaining in the clay after the burn could be made. Since an undeterminable amount of oxygen was given off as gas in the natural balancing of SO_3 and SO_2, calculation cannot be made from the data in hand.

When hydrogen gas was mixed with nitrogen in the atmosphere, a further complication was introduced. There was probably a considerable reaction around 450° to 480° as follows:

$$SO_3 + H_2 = SO_2 + H_2O$$

$$SO_2 + 3H_2 = H_2S + 2H_2O$$

By thus reducing the concentration of SO_3 in the atmosphere, the evolution of more SO_3 was stimulated according to mass law principles. (See Fig. 8.)

TABLE VI

RESULTS OF TREATMENT OF CLAY WITH FERRIC SULPHATE

Time, hours	Temp., °C	Oxygen		200% Excess air		100% Excess air		Nitrogen		90% Nitrogen 10% Hydrogen		
		SO_3	SO_2	SO_3	SO_2	SO_3	SO_2	SO_3	SO_2	SO_3	SO_2	H_2S
1	425	3.48	0.45	1.72	0	2.81	0.45	0.41	1.71	1.39	8.36	0.18
2	445	1.39	0	0.93	0	4.74	0.42	0.54	8.23	3.69	21.34	8.27
3	480	1.93	0.13	0.37	0	0.29	0[1]	0.53	0	0.12	0	3.55
4	510	4.35	1.10	2.64	0	6.08	0.83	2.39	1.93	3.40	13.72	0.67
5	560	4.93	1.58	2.59	0.42	0.28	0[1]	2.21	5.87	0.42	0	0.40
6	615	6.72	5.61	10.43	7.55	16.60	16.16	4.20	11.09	0.82	0	1.22
7	665	3.92	7.18	6.42	6.13	5.88	6.29	3.02	0	0	0	0.87
8	720	3.68	7.72	2.40	0	2.82	3.40	1.26	1.68	0	0	5.68
9	775	5.05	2.00	1.00	0.97	4.50	1.90	....[2]	....	....	....	....
Totals		35.45	25.77	28.50	15.07	43.80	29.45	14.56	30.51	9.84	43.42	20.82
Total per cent sulphur evolved		61.22		43.57		73.25		45.07		74.08		

[1] No CO_2 caught.

[2] 775° attained in 8 hours.

Ferric Sulphate and Coal

When powdered coal was mixed in equal weight with the ferric sulphate added to clay, and the clay burned in pure oxygen, the result was surprisingly simple. The coal all burned out during the first two hours to CO_2, and either contributed a little SO_2 itself or decomposed a very little ferric sulphate. After that, conditions were the same as in the experiment without coal.

When CO_2 was also passed, however, the situation was very different. The coal then burned more slowly to form CO in the presence of the CO_2, and, failing, a ready supply of oxygen attacked and decomposed the ferric sulphate to form SO_2. A possible reaction would be:

$$Fe_2(SO_4)_3 + 3C = Fe_2O_3 + 3CO + 3SO_2$$

or

$$Fe_2(SO_4)_3 + 3CO = Fe_2O_3 + 3CO_2 + 3SO_2$$

Consequently, over 30% of the sulphur was given off as SO_2 in the second hour. The evolution of SO_3 was also a little greater than before in the second hour, due to some of the SO_2 oxidizing to restore the proper balance and to the extra heat generated by the burning coal. During the last three hours the evolution of sulphur appears to be less than before. This decrease, however, is only relative to the amount of sulphur remaining in solid form.

When the oxygen supply is further decreased, much the same sort of action takes place, but more slowly and more nearly completely. The burning of the carbon is spread over the second and third hours, and 37.78% of SO_2 is liberated during this period. It has already been shown that it would take three hours to supply enough oxygen to burn this amount of coal, so it would be expected that the reaction would proceed more slowly and with a greater proportion of SO_2 formed, as is found. The decrease in SO_3 evolution would also be explained by the law of mass action. When there is a deficiency on one side of a balanced action the action tends to make up that deficiency. In the reaction

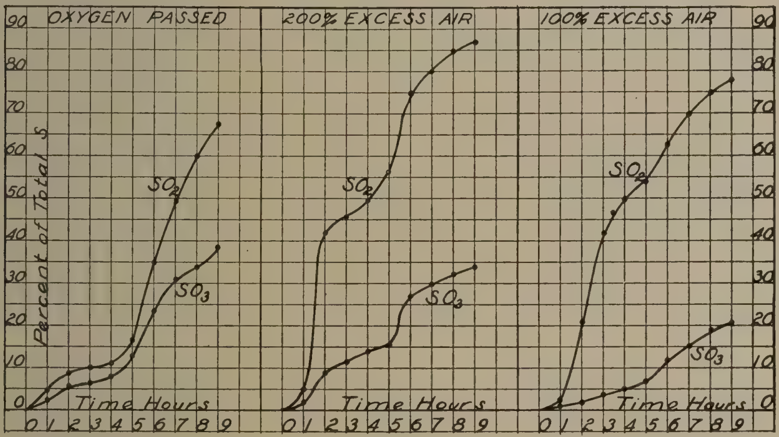

FIG. 9.—Ferric sulphate and coal.

$$2SO_2 + O_2 \rightleftarrows 2SO_3$$

if there is less oxygen present there will be a tendency for the reaction to run to the left and make more oxygen.

The greatest amount of SO_3 evolved is in the sixth hour in all of these three experiments, as it was in the similar three without coal. This would indicate that there was no very radical difference in them. (See Fig. 9.)

TABLE VII

RESULTS OF TREATMENT OF CLAY WITH FERRIC SULPHATE AND COAL

Time, hours	Temp., °C	Oxygen		200% Excess air		100% Excess air	
		SO_3	SO_2	SO_3	SO_2	SO_3	SO_2
1	425	2.24	1.84	1.83	2.42	0.62	0.77
2	445	3.40	1.39	6.78	30.38	1.16	18.12
3	480	0.82	0	3.68	1.50	1.34	19.66
4	510	1.28	0	2.51	6.90	1.65	6.55
5	560	4.90	0	2.41	0.50	2.03	2.08
6	615	10.53	7.91	1.69	6.80	4.87	3.92
7	665	7.27	7.06	2.88	2.77	3.53	3.15
8	720	3.10	7.70	2.27	2.48	3.80	1.90
9	775	4.50	3.40	1.80	0	1.78	1.05
Totals		38.04	29.30	38.85	53.75	20.78	57.20
Total per cent sulphur evolved		67.34		92.60		77.98	

In reviewing the eight experiments made with ferric sulphate it is evident that the evolution of sulphur gases is greatest in the presence of a reducing agent, and that carbon is a better reducing agent in this case than hydrogen. The carbon works best in the normal kiln atmosphere of 100% excess air, and fortunately these are conditions easy of attainment in kiln practice. Therefore, when working with a clay high in ferric oxide, and containing enough sulphur to make trouble, or when using a high sulphur coal, a little fine coal mixed in the clay will make the sulphur burn off more nearly completely and at a lower temperature.

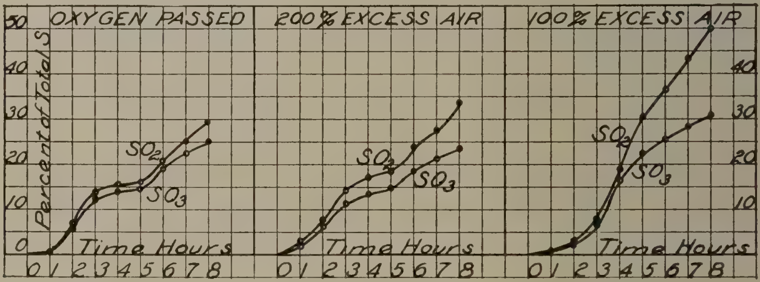

FIG. 10.—Ferrous sulphate.

It will be shown in a subsequent paper of this series that iron oxide in the ware and sulphur from the coal react to form ferric sulphate. A kiln must be held at comparatively low temperature until this sulphur is burned out. These experiments show that addition of a little coal to the ware and an increased oxygen supply should shorten this time of sulphur elimination.

Ferrous Sulphate

Ferrous sulphate was included in this study, not because it was thought that it could exist native in clay, but because it may well be formed as an intermediate product in the decomposition of natural compounds.

Eight burning conditions were studied. It is evident that oxygen is not helpful to the decomposition of the salt and evolution of sulphur. Under identical thermal conditions, with 100% oxygen the yield was 29% of the sulphur added; with 18% oxygen the yield was 33.7%; with 10% oxygen the yield was 50%; with nitrogen alone the yield was 67.6%; and with nitrogen and 10% hydrogen the yield was 53%. (See Figs. 10 and 11.)

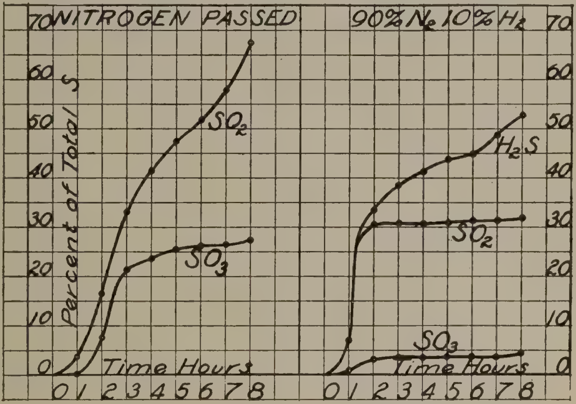

FIG. 11.—Ferrous sulphate.

When lampblack was mixed with the ferrous sulphate in the clay, and burned in pure oxygen, the local heating due to the rapid combustion of the lampblack in the oxygen raised the temperature rapidly, and caused a large evolution of sulphur in the first two hours. After the lampblack had burned out, the evolution of sulphur was slow. With 200% excess air (18% oxygen), the combustion of lampblack would be slower, the local

TABLE VIII

RESULTS OF TREATMENT OF CLAY AND FERROUS SULPHATE

Time, hours	Temp., °C	Oxygen		200% Excess air		100% Excess air	
		SO_3	SO_2	SO_3	SO_2	SO_3	SO_2
1	425	0.27	0	2.25	0.24	0.92	0
2	445	5.39	1.11	3.82	0.72	1.57	0
3	480	6.38	0.18	4.99	2.39	4.40	0.77
4	510	1.93	0	2.50	0	9.64	1.72
5	560	0.65	0	1.26	0	5.86	5.26
6	615	4.45	0	3.83	1.20	2.83	3.60
7	665	3.59	1.33	2.33	0.70	3.20	3.59
8	775	2.71	1.06	2.50	3.85	2.85	3.94
Totals		25.37	3.68	23.58	10.10	31.27	18.88
Total per cent sulphur evolved		29.05		33.68		50.15	

TABLE IX

RESULTS OF TREATMENT OF CLAY AND FERROUS SULPHATE

Time, hours	Temp., °C	Nitrogen		90% Nitrogen 10% Hydrogen		
		SO_3	SO_2	SO_3	SO_2	H_2S
1	425	0	3.69	0.69	6.22	0
2	445	7.62	5.22	2.28	21.44	2.87
3	480	13.77	2.32	0.26	0	4.83
4	510	2.56	6.41	0	0	2.63
5	560	1.61	4.50	0.14	0	2.25
6	615	1.07	3.16	0	0	1.25
7	665	0	5.98	0	0	3.87
8	775	1.07	8.61	0.77	0	4.18
Totals		27.70	39.89	4.14	27.66	21.88
Total per cent sulphur evolved		67.59			53.68	

heating less, and so much oxygen was present that the yield was held down to 43% of the total sulphur.

When 100% excess air was passed (10% oxygen), the lampblack reduced much of the salt, by the reaction,

$$FeSO_4 + C = FeO + CO + SO_2$$

or some similar action, since there was not enough oxygen in the atmosphere to burn the lampblack as fast as it was available. The yield was high, due to the smelting action and the low oxygen content of the atmosphere. (See Fig. 12.)

TABLE X

RESULTS OF TREATMENT OF CLAY AND FERROUS SULPHATE AND LAMPBLACK

Time, hours	Temp., °C	Oxygen		200% Excess air		100% Excess air	
		SO_3	SO_2	SO_3	SO_2	SO_3	SO_2
1	425	3.60	12.67	1.19	8.42	0.54	5.34
2	445	5.02	30.14	3.63	13.88	1.72	48.76
3	480	0.76	0.21	1.30	1.67	1.19	2.10
4	510	0.68	0.33	0.38	0.73	2.75	1.80
5	560	0.96	0.38	0.89	0	0.42	1.00
6	615	1.76	0.49	1.80	0.61	1.65	0.20
7	665	1.90	1.08	1.60	0.67	1.73	1.10
8	775	0.85	1.00	2.18	3.79	0.95	2.10
Totals		15.53	46.50	12.97	29.77	10.95	62.40
Total per cent sulphur evolved		62.03		42.74		73.35	

When ferrous sulphate is burned in pure nitrogen a very interesting study is before us. Unlike the case of ferric sulphate, we have an incompletely oxidized system. Therefore, when there is a tendency for SO_3 to break up into SO_2 and O, the ferrous iron will take up the oxygen instead of its passing off as gas. The normal reaction would be expected to be:

$$2FeSO_4 = Fe_2O_3 + SO_2 + SO_3$$

Hence there is therefore no tendency to form free oxygen.

In a preliminary experiment it was found that, as might be expected, on drying the clay bar, the ferrous sulphate was drawn to the surface and that it there oxidized in the air. This oxygen thus taken up interfered with any calculations that could be made. The final form of the experiment consisted in enclosing the clay bar in the combustion tube as quickly as possible after it was molded. Nitrogen was passed slowly for a day to "air-dry" the bar. The tube was then heated to about 125°C for another day and night with nitrogen passing. In this way oxidation of the ferrous sulphate was prevented. It was then heated in the regular manner with the results as shown.

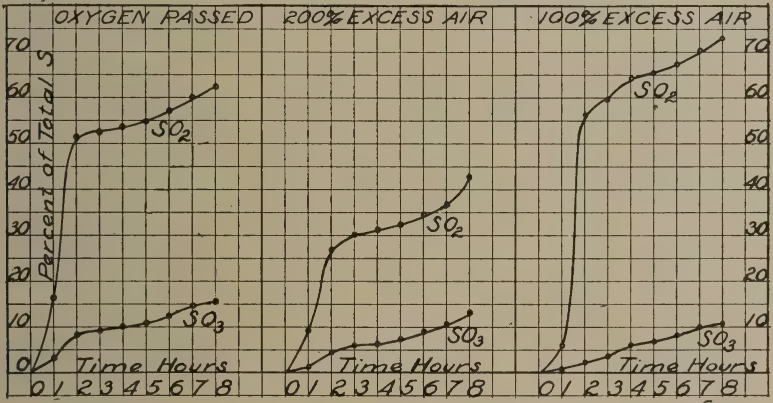

FIG. 12.—Ferrous sulphate and lampblack.

From these results we can calculate the reactions that took place. There was put into the bar 0.3659 gram of iron, 0.2090 gram of sulphur, and 0.4181 gram of oxygen in combination. According to the above reaction, if it ran to completion, there would be 0.1045 gram of sulphur and an equal amount of oxygen combined, and 0.2090 gram of SO_2 evolved; 0.1045 gram of sulphur and 0.1568 gram of oxygen would combine to form 0.2613 gram of SO_3, and the 0.3659 gram of iron would combine with the remaining 0.1568 gram of oxygen as Fe_2O_3. However, the reaction was not completed.

In the actual experiment there was 0.1668 gram of SO_2 formed from 0.0834 gram each of sulphur and oxygen. There was 0.1448 gram of SO_3 formed from 0.0579 gram of sulphur and 0.0869 gram of oxygen. There was therefore left in the clay 0.0677 gram of sulphur and 0.0910 gram of oxygen in addition to the Fe_2O_3. The following statement will help clarify this point:

THEORETICAL COMPLETE DECOMPOSITION	Fe, gram	S, gram	O_2, gram
Put into bar	0.3659	0.2090	0.4181
Evolved as SO_2	. .	0.1045	0.1045
Evolved as SO_3	. .	0.1045	0.1568
Left as Fe_2O_3	0.3659	. .	0.1568
Undecomposed	0	0	0

ACTUAL PARTIAL DECOMPOSITION	Fe, gram	S, gram	O_2, gram
Put into bar	0.3659	0.2090	0.4181
Evolved as SO_2	. .	0.0834	0.0834
Evolved as SO_3	. .	0.0579	0.0869
Left as Fe_2O_3	0.3659	. .	0.1568
Undecomposed	. .	0.0677	0.0910

"Undecomposed" is perhaps not quite the right term, for this sulphur and oxygen no longer exists as ferrous sulphate. A test of the burned bar shows no water-soluble sulphur present. This point will be discussed later.

Ferrous and Ferric "Sulphites" and "Thiosulphates"

These four "compounds" are not well recognized in chemistry, and it was well understood that none of them probably could exist in a natural clay; but it was not impossible that one of them might be formed as an intermediate decomposition product of some naturally occurring iron-sulphur compound. A study of results already obtained indicated that some intermediate sulphur compound was being formed in varying amount under different conditions, and was being "fixed" in the clay. It was with the hope of identifying this compound that the decomposition of every possible combination of iron with sulphur and oxygen was studied in an atmosphere of nitrogen.

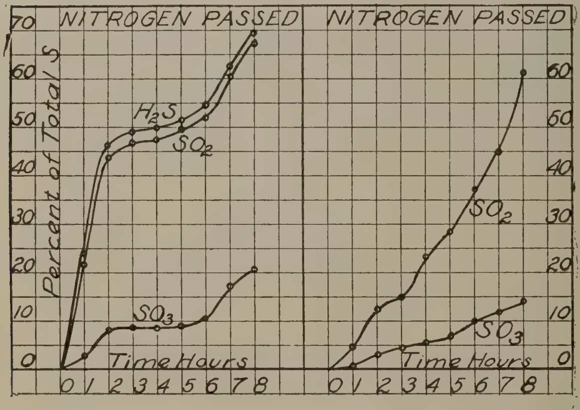

FIG. 13.—Ferrous and ferric "sulphites."

The compounds were given an opportunity to form in the experiments by combining in a clay bar the proper weights of either ferric oxide or siderite, ferrous carbonate, with sodium sulphite or sodium thiosulphate. A study of the evolution of sulphur gases brought out the extent to which the combination had been effected. (See Fig. 13.)

TABLE XI

RESULTS OF TREATMENT OF CLAY AND FERRIC OXIDE OR FERROUS CARBONATE WITH SODIUM SULPHITE

Time, hours	Temp., °C	$Fe_2O_3 + Na_2SO_3$ Nitrogen			$FeCO_3 + Na_2SO_3$ Nitrogen		
		SO_3	SO_2	H_2S	SO_3	SO_2	H_2S
1	425	0.51	4.33	0	2.78	18.70	2.07
2	445	2.57	4.75	0	5.13	17.20	0.10
3	480	1.40	1.35	0	0.36	2.70	0
4	510	1.04	7.51	0	0.37	0.40	0
5	560	1.09	3.91	0	0.20	1.35	0
6	615	3.34	5.45	0	0.88	1.91	0
7	665	1.38	6.21	0	7.20	1.22	0
8	775	2.60	14.40	0	3.61	13.17	0
Totals		13.93	47.55	0	20.53	56.65	2.17
Total per cent sulphur evolved		61.48			79.35		

Sulphites in Nitrogen

As these experiments were at first conducted, H_2S was not expected nor tested for. It appeared difficult to interpret the results obtained, since more oxygen was evolved than could be reasonably accounted for. The experiments were then repeated, testing for H_2S. With ferrous carbonate and sodium sulphite, 2.17% of H_2S was found, 56.65% of SO_2, and 20.53% of SO_3, a total of 79.35% of the sulphur. With ferric oxide and sodium sulphite, no H_2S was found, and 13.93% of SO_3 and 47.55% of SO_2. The expected reactions were:

$$6FeCO_3 + 6Na_2SO_3 + H_2O = 3Fe_2O_3 + 6Na_2CO_3 + H_2S + 5SO_2$$

and

$$Fe_2O_3 + Na_2SO_3 = Fe_2O_3 + Na_2O + SO_2$$

Any SO_3 that was formed could only be accompanied by an equal amount of H_2S. It would, however, be possible for the SO_3 thus formed to be temporarily held back. It did not seem possible that SO_2 could reduce either Fe_2O_3 or CO_2. Accordingly, another source of oxygen must be sought, and this was found in the drying of the clay bars. In a current of air at 110°C, Na_2SO_3 will take up oxygen, the amount depending upon the degree of wetness of the clay when put into the drier. This would account for the inability to check results.

It was evident, due to the decomposition of sodium sulphite at low temperature, that no iron compound was formed. It was therefore considered not worth while to carry the investigation of these compounds any further.

Thiosulphates

From the two bars to which sodium thiosulphate was added, all of the sulphur was burned off. The total sulphur evolved amounted to 99.71%

of the amount added in the case of ferric iron and 100.12% in the case of ferrous iron. (See Fig. 14.) These deviations from the theoretical are within the limit of accuracy of the experiment, and this makes it comparatively simple to study the mechanism of the reactions. We can divide sodium thiosulphate into parts as follows: Na_2O, not affected by heating; S_2O_2 decomposed and evolved as gases; and H_2O (water of constitution of clay), decomposed. The Na_2O we need not consider. In the case of ferric thiosulphate there was present 0.3186 gram of sulphur combined with 0.1593 gram of oxygen; 0.1137 gram of sulphur was evolved as H_2S with the decomposition of water, the sulphur combined with 0.0071 gram of hydrogen, by decomposition of water, thus liberating 0.0563 gram of oxygen. Adding this to the oxygen already combined with sulphur makes 0.2156 gram of oxygen available; 0.1812 gram of sulphur combined with an equal weight of oxygen to form SO_2; 0.0226 gram of sulphur combined with 0.0340 gram of oxygen to form SO_3. The sum of the two weights of oxygen 0.1812 + 0.0340 = 0.2152 gram. This figure checks with the amount of available oxygen given above 0.2156 gram. The agreement of these two figures is even closer than might be anticipated. This may be tabulated as follows:

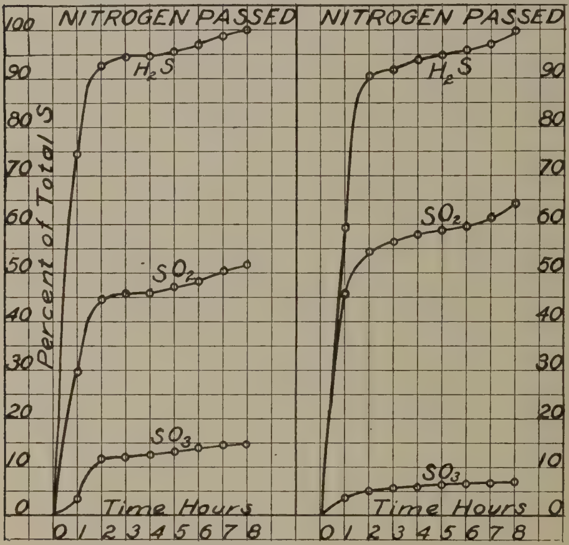

FIG. 14.—Ferrous and ferric "thiosulphates."

	Sulphur available, gram	Sulphur evolved, gram	Oxygen available, gram	Oxygen evolved, gram
Put into clay	0.3186	..	0.1593	..
As H_2S	..	0.1137	0.0563	..
As SO_2	..	0.1812	..	0.1812
As SO_3	..	0.0226	..	0.0340
Totals	0.3186	0.3175	0.2156	0.2152

The calculation shows that the Fe_2O_3, a potential source of oxygen, was not drawn upon at all. Sulphur at 400° to 450°C will decompose water rather than deoxidize Fe_2O_3 in the least degree.

In the case of "ferrous thiosulphate" an even more striking conclusion is reached. Here $FeCO_3$ and $Na_2S_2O_3 + H_2O$ were combined and heated. We can disregard CO_2 and Na_2O as not entering into the rest of the reaction. There was present 0.2440 gram of Fe combined with 0.0698 gram of oxygen and 0.2787 gram of sulphur combined with 0.1394 gram of oxygen. Of this sulphur, 0.1351 gram formed H_2S, combining with 0.0084 gram of hydrogen from water, thus liberating 0.0675 gram of oxygen. This makes a total of 0.2767 gram of oxygen available; 0.1025 gram of sulphur combined with an equal weight of oxygen to form SO_2; 0.0414 gram of sulphur combined with 0.0621 gram of oxygen to form SO_3. This accounts for 0.1646 gram of oxygen. To convert the 0.0423 gram of FeO to Fe_2O_3 requires 0.0349 gram of oxygen. This accounts for 0.2693 gram of oxygen as against 0.2767 gram calculated as available, a good check. This is summarized as follows:

	Iron	Sulphur available, gram	Sulphur evolved, gram	Oxygen available, gram	Oxygen evolved, gram
Put into clay as FeO	0.2440	..	..	0.0698	..
Put into clay as S_2O_2	..	0.2787	..	0.1394	..
Evolved as H_2S	..	..	0.1351	0.0675	..
Evolved as SO_2	..	..	0.1025	..	0.1025
Evolved as SO_3	..	..	0.0414	..	0.0621
To form Fe_2O_3	..	..	..	..	0.1047
Totals	0.2440	0.2787	0.2790	0.2767	0.2693

The close agreement of these two last figures brings out the fact that between 400° and 450°, when a ferrous salt, sulphur, and water are present, the oxidation of ferrous to ferric oxide will go to completion, even though water is decomposed and H_2S is formed. (See Fig. 14.)

TABLE XII

RESULTS OF TREATMENT OF CLAY AND SODIUM THIOSULPHATE AND FERRIC OXIDE OR FERROUS CARBONATE

		$Fe_2O_3 + 3Na_2S_2O_3$			$FeCO_3 + Na_2S_2O_3$		
Time, hours	Temp., °C	SO_2	Nitrogen SO_2	H_2S	SO_3	Nitrogen SO_2	H_2S
1	425	3.87	41.73	14.00	2.98	26.68	44.45
2	445	1.15	7.77	21.70	8.53	5.97	4.05
3	480	0.38	1.30	0	0.34	1.15	0
4	510	0.58	1.15	0	0.23	0	0
5	560	0.32	0.40	0	0.92	0.42	0
6	615	0	0.95	0	0.43	0.58	0
7	665	0.33	1.10	0	0.89	1.20	0
8	775	0.48	2.50	0	0.55	0.75	0
Totals		7.11	56.90	35.70	14.87	36.75	48.50
Total per cent sulphur evolved		99.71			100.12		

Residual Sulphur

One of the most striking features of this series of results is that, in many cases, far from the entire amount of sulphur is evolved at a temperature of 775°C. It is evident that holding at this temperature indefinitely would not liberate the remaining sulphur. This was shown by the experiments in the first paper of this series. The amount of this residual sulphur varies both with different compounds and with different atmospheres. The question naturally arises: Why is this sulphur not evolved and in what form does it exist?

It is felt that a complete answer to this question will be of the utmost value to the ceramic industries. There are two principal factors which retard the operation of an industrial kiln—namely, the evolution of water, and the oxidation of sulphur. Until these two processes are completed the temperature of the kiln may not be advanced beyond certain points without damage to the ware. Many superintendents have worked by rule of thumb, by repeated trial and observation, until they have developed as rapid a heating schedule as they dare use. It may well be, however, that a scientific knowledge of the chemical reactions involved will allow them to shorten their schedule in some way or enable them to produce a superior product. By this means the manufacturer would produce more ware with the same equipment, reducing overhead expense; he would use less coal per unit of ware, promoting conservation; and he would be able to produce at a lower cost, pleasing the public and increasing the demand for ceramic wares.

The question cannot be answered in a few words, nor can the solution be discovered by a few experiments. Its study was begun by selecting some of the burned clay bars which had given the lowest yields of sulphur, breaking out a section in the center, grinding this fine, and weighing out a 10-gram sample of each bar. These samples were then extracted with 500 cc. of boiling water each for half an hour. The water was then decanted and filtered until perfectly clear, then tested for sulphate. The residue was then extracted once more with dilute aqua regia, and the filtered extract tested for sulphate. In neither case, from any of the bars, was as much as 1 per cent of the sulphur originally put into the bar thus extracted.

The conclusion must be drawn that something strange has happened. All of the familiar compounds of iron and sulphur are apparently either soluble in water, such as those containing oxygen, or at least are soluble in boiling dilute aqua regia, such as sulphide, pyrite, etc.

A third extraction was then tried, using a mixture of dilute nitric and hydrofluoric acids in a platinum dish, and evaporating on a steam bath. The nitric acid was added to oxidize any SO_2 which might be liberated, or otherwise evolved, to H_2SO_4. This would not be vaporized at this temperature. The technique of this process of extraction has not as yet been developed to give complete satisfaction. Quantitative results, therefore, can not be given here. Preliminary work, however, points to at least a large proportion of the residual sulphur being rendered soluble in water by this treatment. A plausible explanation concerning this sulphur is as follows.

When any compound of iron and sulphur, with or without oxygen, starts to decompose with heat, it is momentarily in an unstable condition. To use terms of plain, old-fashioned chemistry, some of its bonds of attraction are temporarily unsatisfied. They will satisfy themselves by combining with whatever is present that best suits them under the existing condition. It happens that at just about this temperature the kaolinite molecule is profoundly disturbed by splitting off of water. It may well happen that a combination may form between a partly oxidized iron-sulphur compound or radical, and silica. (Justification for the suggestion that such a compound may be formed is found in the ease with which both silica and iron enter into the formation of complex molecules.) An idea of the difficulty of determining the composition of such a complex compound can be had by a survey of the number of complex silicates. It may well happen that a series of such compounds is formed.

The first clue is the fact that compounds of ferrous iron and silica are, in general, easily fusible. This would indicate that the compound carried ferrous rather than ferric iron. This suspicion is strengthened by the low yield of sulphur evolved when ferrous sulphate was heated in oxygen. This would indicate that $FeSO_4$ was close to the composition of the combining radical. The unoxidized ferrous compounds—sulphide and pyrite—yielded the least sulphur as gases when conditions were only slightly oxidizing. This would seem to indicate that the radical was an incompletely saturated one. When ferrous sulphate was heated in nitrogen, an excess of SO_3 over SO_2 was given off during the first three hours. This might indicate the formation of some compound that is lower in oxygen content than $FeSO_4$. For example: $FeSO_3$ might be formed and be disappearing from the sphere of reaction as a complex with a silicate. Above 500°C the tendency is the other way, and SO_2 comes off in excess. It is possible that the iron compound forming the complex is wanting to oxidize and is reducing SO_3 to SO_2. If so, this oxidation has progressed beyond the ratio of $FeSO_4$, for residual sulphur and oxygen are in the ratio of a mixture having about the proportions $6FeSO_4$, $Fe_2(SO_4)_3$. The general term of "ferrous sulpho-silicate" may be tentatively applied to this complex.

All of this is, so far, little more than speculation. However, results so far prove:

1. That the reactions for the evolution of sulphur from an iron-sulphur compound in clay are generally complex.

2. That not all of the sulphur is given off as gas at temperatures at which the well known iron-sulphur compounds decompose.

3. That the amount of sulphur that is not evolved varies for different compounds and for the same compound in different atmospheres.

4. That the sulphur remaining in the burned clay is in the form of a compound insoluble in water or in dilute aqua regia, as were the compounds in which the sulphur was introduced.

Application to Industry

How does ferrous sulpho-silicate interest the ceramic manufacturer? It may be of vital interest to many. When sulphur gets bound up in a silicate molecule it is not easily decomposed by heat. A temperature is eventually reached, however, when the compound is decomposed, perhaps rather suddenly. If, at this temperature, the ware is approaching vitrification and has a low porosity, and if the volume of sulphur gases is considerable, the gas may not be able to get out as fast as it is formed. Under such conditions a gas pressure develops inside the viscous ware, and consequently the ware swells. Oxygen cannot penetrate against this current of gas, consequently the iron remains in the ferrous state, at least in part, and forms black ferrous silicate. This is the familiar "black core."

It is to avoid the production of bloated and cored ware that the ceramic manufacturer must heat his kilns slowly. The more we know about ferrous sulpho-silicate the better we will know how to prevent the formation of unsalable products. In a subsequent paper the formation of this compound will be discussed from a different point of view.

U. S. Bureau of Mines
Lord Hall, Ohio State University
Columbus, Ohio

THE DEAD BURNING OF DOLOMITE—V[1]

By James Thomas Robson and James R. Withrow

Burn No. 5

The material calcined in Burn 4 was broken in the jaw crusher and run through the disc pulverizer, being ground to the following degree of fineness:

Mesh	Per cent residue
20	None
40	13
80	30
100	27
150	8
Fines	22

The feasibility of various bonds for use of the calcined material was tried in this burn. The burning curve of Burn 4 was followed throughout except that the temperature was taken to cone 18 down rather than cone 17 down as in Burn 4. This was done in order to bring an even heat throughout the kiln. At cone 17 down, one side was hotter than the other, which had cone 17 deformed to about 2 o'clock.

The methods of preparation of bricks for this burn, together with their drying and burning results, follow. All linear shrinkages given are on the original length basis.

Starch Paste as a Bond

A very thick starch paste was made by adding a slip of starch in cold water to boiling water and thoroughly stirring.

Bricks SA14 and S1A14.—These bricks were made of calcined A14 composition to which was added just enough of the starch paste to make it possible to be molded. Brick SA14 was tamped into the mold by hand. Brickette S1A14 was not a standard size brick as was SA14 but simply a one-inch bar about six inches long molded by hand. These bricks formed very well in the molds, but cracked badly upon drying so that they were not burned.

Brick SA14C.—This brick was made of 2,300 grams calcined A14C composition, using 650 grams of starch paste as a binder, and pressed into a standard size brick at 480 pounds per square inch pressure. It pressed and formed very well, but upon drying cracked badly throughout.

It thus appears to be impossible to use starch paste as a bond for calcined A14 composition because of cracking upon drying.

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[1] Published by permission of the Director, U. S. Bureau of Mines. See "The Dead Burning of Dolomite," *Jour. Amer. Ceram. Soc.*, **7** [1], 61; [2], 141; [3], 207; and [4], 300 (1924).

Magnesium Chloride Solution as a Bond

Brick MA14.—Made of calcined A14 composition using a saturated solution of $MgCl_2$ as a tempering medium, enough solution being added to make the mixture soft and plastic so that the brick was made by the soft-mud process. It dried without cracking and burned very well except for a few cracks on the bottom. (See Fig. 38.) The linear expansion from plastic to burned was 1.25%.

Brick M1A14.—To 2,000 grams of A14 calcine were added 400 cc. of a 23% $MgCl_2$ solution. This brick was pressed with 460 pounds per square inch pressure. It cracked badly on drying, was rescreened, and, after adding a large excess of the $MgCl_2$ solution it was formed by the soft-mud process. This trial did not crack on drying, but cracked very badly during burning.

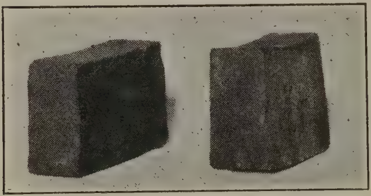

Fig. 38.—Bricks NaD_9 and MA_{14}.

Brick M2A14.—Made by using calcined A14 composition plus 23% of $MgCl_2$ solution and soft-mud process. This brick cracked on drying and was not burned.

It appears necessary to use a saturated solution of $MgCl_2$ as a tempering medium, otherwise if a dilute solution is used, the bricks crack on drying.

Caustic Magnesia as a Bond

Caustic magnesia of the California variety, made for use in stucco work, was used.

Brick EA14.—This brick consists of calcined A14 composition, 90% by weight plus 10% of caustic magnesia by weight. These were thoroughly mixed and screened. Then sufficient water was added to mold it by the soft-mud process. This brick cracked badly on drying. No bonding effect whatever seemed to be exercised by the caustic magnesia present, so that this method was discarded and the brick not burned.

Sorrel Cement as a Bond

An attempt was made to produce Sorrel cement in the calcined dolomite and thus insure a firm bond. This was attempted by using caustic magnesia and $MgCl_2$ solution as shown below.

Brick M3A14.—Made by using calcined A14 mixture weighing 1,000 grams, 300 grams of a 14° Bé. $MgCl_2$ solution and 50 grams of caustic magnesia. This mixture was thoroughly tempered by hand and molded by tamping the mixture in the mold. The brick formed well but cracked badly on drying and was not burned.

The reason for cracking was probably due to the presence of sufficient free lime in the calcine to cause the Sorrel cement to disintegrate, as explained by Bole and Shaw.[1] These men state that free lime even in amounts under 2% is detrimental to the life of an oxychloride cement and in quantities over 3% causes early disintegration.

Sodium Silicate as a Bond

A solution containing 25% of dry sodium silicate by weight was mixed further with water so that the resulting solution contained 4.5% dry sodium silicate by weight.

Brick NaA14.—Made of calcined A14 composition tempered with sufficient sodium silicate solution so that the resulting percentage of dry sodium silicate on the A14 calcine weight basis amounted to 0.62%. This brick was molded by hand. It cracked badly on drying and was not burned.

Brick NaD9.—Made of D9 composition using sufficient solution to give 0.80% dry sodium silicate. This brick was molded by hand and dried and burned very well. (See Fig. 38.) The brick expanded 1.25% from plastic to burned.

It appears that D9 composition may not be susceptible to this action of cracking during the drying process as is A14 composition.

Gum Arabic as a Bond

Brick FA14.—A thick emulsion of gum arabic was formed by warming an excess of the gum with water. This was cooled and when added to calcined A14 material, it formed small, hard lumps immediately, which made the mass impossible to mold. This material was then heated until it became soft and was then molded by hand. This brick cracked badly immediately upon cooling and was not burned.

Molasses as a Bond

The heavy "second molasses" obtained from cane sugar was used as a bond.

Brick BA14.—This brick was made using 300 grams of molasses to 1,300 grams of A14 calcine. After thorough mixing, a brick was hand molded, which dried and burned very well. (See Fig. 39.) The linear expansion amounted to 1.25%.

Brick B1A14.—Made of A14 material using 450 grams of molasses to 2,000 grams of A14 calcine. This molasses was thoroughly mixed throughout and the mixture then pressed at 550 pounds per square inch. The brick formed was very firm and solid. No cracking occurred upon drying at 50°C. It burned very well, but shrunk slightly less on the edge in contact with the magnesite brick support. (See Fig. 39.) The linear shrinkage was 9.3%.

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[1] "Caustic Calcination of Dolomite and its Use in Sorrel Cements," *Jour. Amer. Ceram. Soc.*, **5** [11], 816 (1922).

Brick B2A14.—This brick was formed of A14 calcine plus molasses and a volume of water equal to that of the molasses. When the water was added to this mixture, it immediately formed small hard lumps. After breaking up the lumps and thoroughly tempering, a brick was tamped in the mold by hand. This brick swelled to a much larger size upon drying and completely disintegrated when an attempt was made to remove it from the mold.

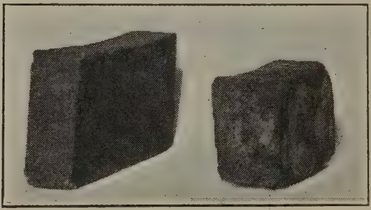

Fig. 39.—Bricks BA_{14} and B_1A_{14}.

Bricks B3A14, B4A14, and B5A14.—Those bricks which cracked on drying namely: SA14, S1A14, SA14C, M2A14, M3A14, EA14, NaA14, FA14, and B2A14 were again ground through the rolls and made into bricks using molasses as a bond. These bricks were made using 515 pounds per square inch pressure. They did not crack upon drying, but cracked during the burning process. This cracking was probably due to the fact that the previous bonds containing much water were not driven out before adding the molasses and although no cracks were noticed upon drying after adding molasses, nevertheless the water was still present and strains may have been set up both in the drying and burning process. These bricks were dried over night at 50°F.

Dextrin as a Bond

Brick DD6.—Made of 1,500 grams of calcined D6 composition, using 50 grams of thick dextrin paste formed by mixing equal parts of corn dextrin and flour in boiling water until a thick paste was formed. The 50 grams of paste was mixed with 150 cc. of water and after mixing throughout the D6 calcine by hand, was pressed into a brick using 480 pounds per square inch pressure. This brick formed, dried, and burned very well. (See Fig. 40.) Its linear shrinkage was 11.4%.

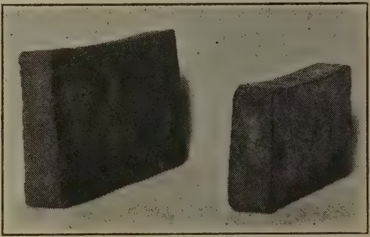

Fig. 40.—Bricks DD_6 and R_6A_{14}.

Raw Material for Calcine

Bricks R6A14 and R7A14.—These bricks were made of composition A14 using raw dolomite (100-mesh) plus C.P. fluxes and mixed with sufficient water to make a very thick slip. They were formed in a standard size wooden mold. These bricks dried in very good condition. R6A14 burned well, similar to brick R3A14 in Burn 3. (See Fig. 40.) It had 28.0 % linear shrinkage. R7A14 fell over against a silica brick and fluxed with it.

Bricks R1A14C and R2A14C.—These were made of raw 100-mesh dolomite plus the commercial fluxes including North Carolina kaolin similar to composition A14C.[1] R1A14C was molded by the soft-mud process. It dried and burned well except for a small crack clear through the brick. (See Fig. 41.) Brick R2A14C was pressed, using 498 pounds per square inch pressure. It dried very well, but developed three large cracks on burning. The linear shrinkage for R1A14C was 25.7%. The linear shrinkage for R2A14C amounted to 25.7% also.

FIG. 41.—Bricks $R_1A_{14}C$ and $RA_{14}G$.

Bricks RD6 and R1D6.—These bricks were made of raw D6 composition. RD6 was pressed at 535 pounds per square inch pressure and R1D6 was hand molded. Both dried well, but cracked rather badly on burning, especially R1D6.

Brick X15A14.—Made of composition similar to bricks X13A14 and X14A14 as given earlier in this paper.[2] This brick dried well, but cracked badly and was glossy due to overfiring at cone 18.

Use of Gouverneur Dolomite

In order to determine whether or not other forms of magnesite could be dead burned the same as that from Cedarville, a batch of A14 composition was made using C.P. fluxes and a metamorphosed dolomite or marble from Gouverneur, St. Lawrence County, New York.

The composition of this dolomite, as determined by Bole and Shaw[3] is as follows:

$MgCO_3$	43.32
$CaCO_3$	55.21
SiO_2	1.00
R_2O_3	0.46
	99.99

The dolomite was ground to pass a 100-mesh screen, mixed with fluxes, etc., in the same manner as described in the preparation of A14 composition.

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[1] *Jour. Amer. Ceram. Soc.*, **7** [4], 308 (1924).

[2] *Loc. cit.*, **7** [4], 307 (1924).

[3] *Ibid.*, **5** [11], 819 (1922).

Although no sulphur is given in the analysis, the sample evidently contained traces of it, the odor of which could be detected as H_2S when the sample was broken in the jaw crusher. During crushing a very bright, distinct luminescence similar to the well-known triboluminescence of sphalerite was distinctly visible.

Brick RA14G.—Unlike the mixture of A14 using Cedarville dolomite, this Gouverneur dolomite mixture was not sufficiently plastic to be molded by the soft-mud process. A brick was made using this A14 composition pressed at 535 pounds per square inch pressure. This brick formed, dried, and burned very well. (See Fig. 40.) It had a linear shrinkage of 28.0%. The appearance of this brick was the same as those of A14 composition made from Cedarville dolomite and after two months' exposure it has remained unchanged.

Thus it appears probably true that any pure dolomite can be dead burned by this process.

Summary of Satisfactory Brick in Burn 5

This burn shows that suitable bricks when burned to cone 18 down may be made as follows:

1. Calcined D9 composition plus 0.8% sodium silicate. Hand molded.
2. Calcined A14 composition plus 23% of molasses by weight. Hand molded.
3. Calcined A14 composition plus 22.5% of molasses by weight. Pressed at 550 pounds per square inch.
4. Calcined D6 composition plus 13% by weight of a 25% dextrin, 75% water mixture. Pressed at 480 pounds per square inch pressure.

Burn 6

Magnesite brick are burned while standing on end in order to overcome the lower shrinkage of the edge in contact with the supporting brick. When burned while standing on the 9″ x $2^1/_2$″ edge, magnesite brick always shrink less on the edge in contact with the supporting brick and also crack throughout on this edge, so that Burn 6 was made having the dolomite bricks standing on end in order to overcome this distortion noted in Burn 5, where the bricks were burned while supported on edge.

Bricks made of calcined A14 composition, mixed with molasses and burned to cone 17 down in 52 hours are shown in Fig. 42.

Brick FA14.—This brick was made of calcined A14 composition, which was ground to give the following screen analysis. (See following page.)

This ground material was pressed into a brick $2^7/_{16}$″ x $4^3/_8$″ x $8^3/_4$″, using 554 pounds per square inch pressure and 14% of molasses as a binder.

Upon burning to cone 17 down, the brick warped very slightly. It was slightly fused to the magnesia brick on which it stood and shrunk $^1/_4$ inch less on this end than on the upper end. The edges were very sharp and distinct, showing little or no fusion. The volume shrinkage was 16%, most of which was no doubt due to expulsion of the molasses rather than shrinkage due to vitrification. This brick was very solid and firm, having a sharp ring; the only possible objection being the slightly less amount of shrinkage on the supporting end. (See *a*, Fig. 42.)

Mesh	Per cent residue
8	8.0
12	20.6
20	20.0
80	32.0
100	5.4
Fines	14.0
	100.0

Brick HA14.—This brick was made of calcined A14 composition ground as follows:

Mesh	Per cent residue
20	0
40	18.0
80	59.0
100	5.4
Fines	17.6
	100.0

This ground material was pressed into a brick $2^{11}/_{16}'' \times 4^3/_8'' \times 8^3/_4''$, using 554 pounds per square inch pressure and 35% of molasses as a binder. This molasses was in excess to what was actually necessary for bonding purposes.

When burned to cone 17 down, this brick did not warp but again shrunk $^1/_4$ inch less on its supporting end. The edges were very sharp and distinct. The volume burning shrinkage was 25%. This shrinkage is high because of the high content of molasses used. This brick was very firm and solid, having a sharp ring. (See *c*, Fig. 42.)

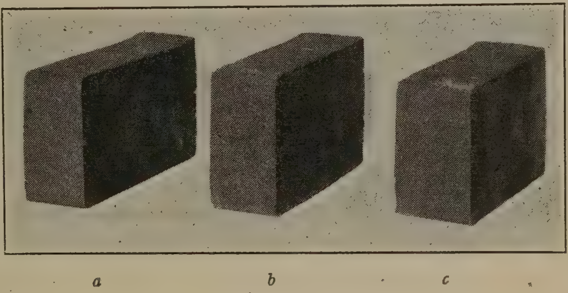

FIG. 42.

Brick IA14.—This brick was made of calcined A14 composition, the same as used in Brick HA_{14}. The green brick measured $2^7/_{16}'' \times 4^3/_8''$ x

$8^3/_4''$. It was pressed at 554 pounds per square inch pressure, using an unweighed amount of molasses, enough being added to easily work up the batch. This brick fused slightly to the magnesia brick on which it was supported and shrunk $^1/_4$ inch less on the supporting end. The edges were very sharp and distinct, showing no fusion. The volume shrinkage was 29%. The brick was very solid and firm, having a good ring. (See *b*, Fig. 42.)

Discussion of Burn 6

All three bricks are very good except for the smaller amount of shrinkage on the supporting end. Brick FA_{14}, using coarser grained material, warped slightly. Bricks HA_{14} and IA_{14}, using finer material, did not warp.

Only those bricks made using molasses as a binder were found to fuse to the magnesia brick. It is believed that this is due to the fact that during the early stages of the burn the molasses gradually seeps down through the brick and runs into the pores of the magnesia supporting brick. This molasses carries a small amount of dolomite with it into the magnesia brick which at higher temperatures causes the slight fusion noted with the magnesia. It was possible to knock these bricks off the magnesia bricks by tapping with a hammer, but a small, skin-like portion of the dolomite brick came off with the magnesia brick. It is suggested that these bricks be set on powdered magnesia spread over the magnesia or silica brick similar to sanding in an ordinary brick kiln to prevent sticking.

Reasons for Dolomite Stability

An analysis of compositions A14, D6 and D9 made of dolomite plus C.P. fluxes to determine the free CaO or CaO existing therein in the form of possible compounds decomposable by water such as $CaO.Al_2O_3$[1] was made as follows:

The calcined material was crushed and ground to pass a 100-mesh screen. A one-half gram sample was treated with 1,000 cc. of distilled water and thoroughly stirred. This was filtered and the residue washed with distilled water until all traces of calcium were removed. The calcium present in the filtrate and washings was precipitated by means of ammonium hydroxide and ammonium oxalate and ignited as CaO.

The results were as follows:

	A14	D6	D9
CaO	25.88%	23.44%	19.68%

Thus it is seen that the percentage of free CaO in these calcined dolomite compositions still exists in considerable amounts. The dolomite analysis shows the CaO content to be 30.2%. Since A_{14} contained 10% of flux and 90% of dolomite, the actual content of CaO in A14 before calcination is 90% of 30.2% or 27.18%; hence but 4.8% of the total lime present has been rendered insoluble when A14 composition is ground to pass a 100-mesh screen. Likewise in D_6 composition where 15% of flux is used, the actual lime content before calcination is 25.67% and after calcination is 23.44% so that 8.7% of the total lime present in D6 has been rendered insoluble. A similar calculation shows that 23.3% of the total lime present in D9 has been rendered insoluble by calcination with 15% of flux.

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[1] Van Nostrand's *Chemical Annual*, p. 148 (1918).

Composition D9 which contains 3% Al_2O_3 has more CaO in the insoluble form than D6 which contains no Al_2O_3 except the 0.5% impurity as reported in the analysis which makes the total Al_2O_3 content of D9 equal 3.4%. The SiO_2 content in both is 6%. The Fe_2O_3 content in D6 is 9% and in D9 is 6%. As shown in Fig. 1,[1] there are 4 compounds between CaO and Al_2O_3. Also the fusion tests tend to indicate a strong fluxing action of Al_2O_3 with CaO so that it is probably due to the difference in Al_2O_3 content that there is less free CaO in D9 than in D6. Of the possible compounds which could be formed in these mixtures, $CaO.Al_2O_3$ is the only one that could be found in the literature as decomposable by water; hence, no doubt, at least most of the CaO found by this analysis exists as free CaO in the mixture.

Composition A_{14} contained 4% Al_2O_3 but only 2% Fe_2O_3 and 4% SiO_2 so that it cannot be considered in this method of comparing the action of the different fluxes on D6 and D9.

The slaking of this free lime with water is considered to be the cause of cracking of bricks made from the calcined mixtures when finely ground and tempered with water. A bond tends to overcome this cracking by its binding action, and as shown in bricks DD_6 and NaD_9 which contain less free CaO than does A_{14} composition, they are very successful. It is in all probability due to the low water content of molasses that A14 composition can be successfully made into brick.

The question naturally arises as to why these compositions which appear to contain so much free lime are dead burned and do not slake when in brick form. There are several possible reasons for these phenomena which are given in discussion throughout this work. They are as follows:

1. The condition of approaching the natural composition of Breunnerite is brought about by very intimately mixing the dolomite with Fe_2O_3 and grinding very finely so that the MgO forms the stable periclase when calcined.[2]

2. The large amount of MgO present acts as an adulterant and renders the lime inert.[3]

3. The lime is overburned, that is, it is burned at a very high tempera-

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[1] See "Dead Burning of Dolomite," *Loc. cit.*, **7** [1], 65 (1924).

[2] *Loc. cit.*, **7** [1], 71 (1924).

[3] *Ibid.*, 7 [1], 73.

ture cone 17, approximately 1470°C, in the presence of impurities, notably silica, so that it is rendered inactive. (*Ibid.*, 71.) These phenomena of overburning are also shown by lime treated with insufficient water to complete hydration. The unslaked portion will "burn" and become practically useless.[1]

4. A dense lime slakes more slowly than a porous lime. (*Ibid.*, 73.) The absorption of cubes A_{14}, D_6, and D_9 determined by the vacuum method were 0.47%, 2.5% and 2.4%, respectively; showing that these bodies were well vitrified and impervious to the action of water.

5. Compounds may be formed which form an envelope around these CaO grains and prevent them from slaking. Kowalke and Hougen[2] show that in burning magnesia to 1700°C, forsterite ($2MgO\ SiO_2$) crystals form a complete envelope about periclase crystals.

6. It is a known fact that the top layer of fine lime will air-slake (*i. e.*, form $CaCO_3$) and the crust of inert material so formed will prevent access of the air to the quicklime underneath, making fine lime so stable that it can be shipped in open gondola cars.

7. The stability of hydrated lime is likewise attributed to the fact that an impervious coating of air-slaked lime forms on the outside and prevents access of the air to the interior.[3] Chiefly to this cause is attributed the stability of these dolomite compositions. It is considered that a crust or envelope of calcium carbonate is formed around the small particles of free lime present, preventing their contact with water or air, thus rendering them nonsoluble. When finely ground, this protective coating is broken up and the free lime present thus rendered soluble. As stated, the free or water soluble CaO in the product ground to pass 100-mesh ranges as high as 25.88% in composition A_{14}. This water soluble CaO, at least that which exists as free CaO, is thought to be surrounded by this impervious air-slaked coating of lime, and is thus inaccessible to the action of water and air.

Absorption tests of samples A_{14}, D_6 and D_9 at definite intervals for change in weight when soaked in cold water under atmospheric pressure, after having undergone the absorption test under vacuum for one hour, gave the following results.

After soaking for 24 hours, the water in which the briquettes were immersed gave a faint test for CaO. After soaking for 72 hours, the water still gave but a faint test for CaO. The water was then changed and, after remaining in this water for 48 hours, cube A14 did not change in weight, cubes D_6 and D_9 lost but 0.01 gram in weight. The water gave no test for calcium.

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[1] W. E. Emley, "Manufacture of Lime," U. S. Bureau of Standards, *Tech. Paper* **16,** 77 (1913).

[2] "Crushing Strength of Magnesia-Silica Mixtures at High Temperatures," *Trans. Am. Electrochem. Soc.*, **33,** 215 (1918).

[3] Emley, *ibid.*, 16–7.

After drying these cubes for 24 hours at 110°C, A_{14}, D6 and D9 showed a decrease in weight from that of their original dry weight equal to 0.39%, 0.49%, and 0.42%, respectively. A slight scum, due to calcium carbonate, was visible on their surfaces.

HOURS SOAKED	CUMULATIVE PERCENTAGE INCREASE IN WEIGHT		
	A14	D6	D9
24	0	0	0
48	0	0	0
72	0	0.06	0.16
120	0	0	0.08

Analyses for CO_2, H_2O and water soluble CaO in samples of A14 composition which had just been removed from the kiln and one which had stood in the air for 12 months were as follows:

	New sample A14, per cent	12 months' old sample A14, per cent
CO_2	2.87	6.03
H_2O	1.24	3.39
Water soluble CaO	25.88	23.76
Theoretical CaO	27.18	27.18
Combined or insoluble CaO	1.30	3.42

From the above it is seen that the percentage of CO_2, H_2O, and insoluble CaO has increased over a period of 12 months. This is due to the formation of carbonates with aging. Evidently more lime has gone into the carbonate form which will, therefore, tend to make the brick even more stable, so that instead of slaking upon standing, this brick will become more resistant to slaking. The percentage of H_2O has increased with aging, probably much of this H_2O is hygroscopic water rather than chemically combined water.

If all of the insoluble CaO were present as $CaCO_3$, the 1.3% of insoluble CaO in the new sample of A14 would require 1.02% of CO_2. This leaves an excess of 1.85% CO_2, according to the analysis. Likewise, in the old sample of A_{14}, the 3.42% of insoluble CaO requires 2.69% CO_2, thus leaving 3.34% CO_2 unaccounted for. It is possible that some of the soluble CaO may be present as the bicarbonate $Ca(HCO_3)_2$; also, no doubt, a small amount of CO_2 was left in the product after calcination. Most limestones retain nearly 0.5% of CO_2 after calcination in lime kilns.

General Conclusions

1. In this study, several compositions capable of being calcined at cone 16–17 down, to form apparently dead-burned dolomite, have been found.

2. These stable members together with their compositions are as follows:

Member	Dolomite %	Fe_2O_3 %	Al_2O_3 %	SiO_2 %
B13	90	3.04	5.82	1.14
B15	90	3.62	2.31	4.07
B21	90	....	5.32	4.68
B22	90	....	4.60	5.40
B23	90	....	2.98	7.02
A14	90	2.0	4.0	4.0
A15	90	2.0	2.0	6.0
D6	85	9.0	....	6.0
D9	85	6.0	3.0	6.0
D11	85	5.0	5.0	5.0
D13	85	3.0	9.0	3.0
D15	85	3.0	3.0	9.0
D18	85	....	12.0	3.0
D19	85	....	9.0	6.0

3. Of these members, the following can be classed as Number 1 refractories: *i. e.*, their fusion point lies above standard cone 32, which deforms at about 1770°C; B13, B15, B21, B22, B23, A14, A15, D6, D9, D11, D15 and D19.

4. Any of these compositions could, no doubt, be used as dead-burned granular dolomite.

5. These compositions are made of materials ground to pass a 100-mesh screen and thoroughly mixed before calcination.

6. Composition A_{14} can be made satisfactorily using North Carolina kaolin as a source of the SiO_2 and most of the Al_2O_3.

7. Composition D9 cannot be made using North Carolina kaolin because of slaking due to calcium orthosilicate ($2CaO.SiO_2$) formation.

8. As the percentage of flux increases up through 15%, the number and stability of the calcined dolomite flux mixtures increase.

9. Five per cent of the three fluxes Fe_2O_3, Al_2O_3 or SiO_2 is insufficient to produce a dead-burned product from this dolomite.

10. Dead-burned dolomite cannot be obtained using any one of the three fluxes Fe_2O_3, Al_2O_3 or SiO_2 alone in amounts of 5%, 10%, 15% and 40%.

11. Pure dolomites of different crystalline character can be dead burned.

12. All compositions containing 5% of fluxes have deformation points above cone 32.

13. All compositions containing 10% of fluxes have deformation points above cone 32, except the composition A17 containing 10% of Al_2O_3 alone as a flux which deforms at cone 15.

14. When 15% of the fluxes studied herein are present, compositions with fusion temperatures at cone 20 or lower are obtained when the total Al_2O_3 content exceeds 6% and Fe_2O_3 is present.

15. Al_2O_3 has by far the greatest effect in lowering the fusion temperature of this dolomite. Fe_2O_3 is next and SiO_2 has the least effect on lowering the fusion temperature.

16. These dolomite compositions without molasses will not flux with magnesite below cone 33 as shown by the fusion tests.

17. It is very difficult to make commercial sized bricks of the raw material because of the excessive volume burning shrinkage which at cone 16–17 down, averages about 70% on the dry volume basis. This high shrinkage causes cracking and deformation of the bricks.

18. Using previously calcined dolomite and then adding the fluxes and calcining is of no value because of high shrinkage due to hydrated lime.

19. Dolomite brick can be made satisfactorily as follows:

Calcine the raw materials of the compositions below to cone 17 down. Grind to pass a 20-mesh screen. Form into bricks and burn to cone 17–18 down.

RAW BATCH RECIPE

	A_{14}	D_6	D_9
100-mesh dolomite	90	85	85
Fe_2O_3	2	9	6
Al_2O_3	4	..	3
SiO_2	4	6	6

Method I—A14 composition plus 16%–23% of molasses by weight. Mold by hand or press at 550 pounds per square inch.

Method II—D6 composition plus 13% by weight of a 25% dextrin, 75% water mixture. Press into brick at 480 pounds per square inch.

Method III—D9 composition plus 20% of a 4.5% sodium silicate solution. Mold by hand.

20. When using 100-mesh raw Cedarville dolomite, water serves very well as a bond for a standard size brick.

21. Artificial bonds containing a high percentage of water cannot be used for making bricks of composition A14 because of cracking during the drying stage.

22. Cracking of the fine calcined material during drying is due to hydration of the free lime.

23. Compositions D_6 and D_9 do not appear to have the fault of cracking during drying when much water is used in the bond.

24. Tar appears to be unsatisfactory for bond for the calcined material, although it contains no water.

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(This concludes this paper on "The Dead Burning of Dolomite")

ERRATA

The following corrections in the paper by N. L. Bowen and J. W. Greig, "The System: Al_2O_3–SiO_2," **7** [4], 238 (1924), should be noted:

In title of paper and legends for Figs. 2 and 4, replace . with – "in $Al_2O_3.SiO_2$; as Al_2O_3–SiO_2.

P. 238: Footnote 2 should read "The Best Described Examples Are Those from the Island of Mull. H. H. Thomas, *Quar. Jour. Geol. Soc.,*" etc.

P. 242: Legend, Fig. 4. Omit the words "After Shepherd, Rankin and Wright."

P. 245: Line 4. Table I should read "Table II."

All right-hand page headings to read as follows: "The System: Al_2O_3–SiO_2" instead of "$Al_2O_3.SiO_2$."

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ORIGINAL PAPERS

CLAY SEWER PIPE MANUFACTURE.—IV. THE INFLUENCE OF DIFFERENT SALT GLAZING TEMPERATURES UPON THE COLOR AND GLOSS OF GLAZES OBTAINED ON CLAYS WITH VARYING SILICA, ALUMINA, AND IRON OXIDE CONTENTS[1]

By H. G. Schurecht[2]

ABSTRACT

Object.—A study was made of the effects of different salt glazing temperatures upon the color and brightness of salt glazes produced upon clays with varying silica, alumina, and iron oxide contents.

Results.—In tests conducted in commercial kilns operating under normal conditions, it was found that increasing the salt glazing temperatures has a tendency to produce duller and darker glazes on clays containing iron oxide.

The brightness of the glazes produced may be approximately represented by the following formula:

$$-1.00x_1 + 0.376x_2 - (1.885 + 0.385(1.01253)^{(T-1110)})x_3 = 100G$$

x_1, x_2 and x_3 represent the percentages of silica, alumina and iron oxide, respectively. T is the salt glazing temperature in °C. When G was greater than 0, the glazes were bright; when between -0.1337 and 0 they were semi matt; and when less than -0.1337 they were matt.

The color obtained may be approximately represented by the following formula:

$$10.3x_1 - 2.65x_2 + (14.6 + 54.1\ (1.0066)^{(T-1110)})x_3 = 100C$$

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[1] Published through the courtesy of the Eastern Clay Products Association and the Clay Products Association under whose auspices this work has been done as part of their research program on the manufacture of clay sewer pipe.

[2] Senior Fellow, Mellon Institute of Industrial Research, University of Pittsburgh, Pittsburgh, Pa.

When C was between 0 and 2, white to tan glazes were produced; when between 2 and 3.5, light brown glazes were obtained; when between 3.5 and 4.75, brown glazes were produced; when between 4.75 and 8.2, mahogany colors were obtained; and when above 8.2, dark brown to black glazes were produced.

Clays containing a high iron oxide content should be salt glazed at low temperatures while clays containing a low iron oxide content should be glazed at high temperatures to produce the best glazes. Decreasing the iron oxide and alumina contents will improve the brightness of the salt glazes. High alumina clays will produce darker colors than high silica clays with the same percentage of iron oxide.

Introduction

Where it is not possible to test the strength of sewer pipe the quality of pipe is most commonly judged by their appearance. Sewer pipe with dense bodies and dark brown or mahogany bright glazes are usually selected in preference to lighter colored pipe or pipe with dull rough glazes. Judging the quality of pipe by their color is misleading since pipe of light color may be far superior to certain dark colored pipe, but their less pleasing appearance is, unfortunately, often the cause of their rejection. The density of the body and the brightness or smoothness of the glaze are much better criterion for judging the quality of sewer pipe.

One of the most important methods of controlling the smoothness and color of sewer pipe is by means of their salt glazing temperatures which vary between wide limits. The temperatures at which sewer pipe are now being salt glazed vary from cone 02, 1922°F to cone 10, 2426°F. The temperatures obtained in different portions of the same kiln may vary as much as 10 cones, 360°F. This work was done to determine how much the brightness and color of glazes are affected by different salt glazing temperatures.

Sufficient has already been done to show that it is possible to salt glaze sewer pipe at too low as well as at too high temperatures, depending largely upon the content of iron compounds present and also to a lesser extent upon the contents of alumina and silica in the clay.

Experimental Methods

The 36 synthetic clays previously tested[1] containing varying amounts of silica, alumina and iron oxide were also studied in this work. These three ingredients were varied between the following limits:

Alumina (Al_2O_3)	12.30 to 37.18 per cent.
Silica (SiO_2)	38.41 to 80.95 per cent.
Iron Oxide (Fe_2O_3)	0.33 to 16.40 per cent.

The mixtures were prepared by adding varying amounts of potter's flint and iron oxide to a 1:1 Florida kaolin:Tennessee ball clay mixture.

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[1] "The Effect of Variable Alumina, Silica and Iron Oxide in Clays on Some Properties of Salt Glazes," *Jour. Amer. Ceram. Soc.*, **6** [6], 717–29(1923).

The clays used had compositions approaching closely the analyses of pure clay. In Tables I and II are given the compositions of both the raw and fired samples, respectively. All of the ingredients were screened through a 100-mesh sieve before mixing.

The mixtures were molded into bars which were set in fire clay plaques. These were fired and salt glazed in commercial sewer pipe kilns at cone 02, cone 3, cone 7 and cone 10.

TABLE I

THE CHEMICAL COMPOSITION OF THE RAW MIXTURES

No.	Alumina, Al_2O_3	Silica, SiO_2	Iron oxide, Fe_2O_3	Titanium oxide, TiO_2	Calcium oxide, CaO	Magnesium oxide, MgO	Alkalies $Na_2O + K_2O$	Sulphur S	Water, H_2O
A-1	31.41	38.81	16.30	0.23	0.21	0.02	0.83	0.03	12.20
A-3	23.89	53.65	12.29	0.17	0.16	0.02	0.54	0.02	9.26
A-5	19.80	62.80	9.82	0.13	0.12	0.01	0.41	0.01	7.48
A-7	16.13	68.70	8.17	0.11	0.10	0.01	0.38	0.01	6.31
A-9	13.96	73.20	6.99	0.10	0.09	0.01	0.33	0.01	5.46
A-11	12.30	76.28	6.10	0.08	0.07	0.01	0.30	0.01	4.82
C-1	31.62	39.15	15.73	0.22	0.21	0.02	0.70	0.02	12.39
C-3	24.44	55.02	10.16	0.17	0.15	0.02	0.55	0.01	9.53
C-5	19.63	63.99	8.10	0.12	0.11	0.01	0.44	0.01	7.67
C-7	16.41	69.84	6.71	0.10	0.09	0.01	0.38	0.01	6.41
C-9	14.18	74.21	5.86	0.09	0.08	0.01	0.33	0.01	5.44
C-11	12.47	77.22	4.98	0.07	0.06	0.01	0.30	0.01	4.69
E-1	33.55	41.42	10.68	0.24	0.22	0.02	0.73	0.02	13.12
E-3	25.18	56.25	7.94	0.16	0.10	0.02	0.55	0.01	9.80
E-5	20.07	65.18	6.29	0.12	0.08	0.01	0.45	0.01	7.32
E-7	16.71	70.81	5.22	0.10	0.08	0.01	0.38	0.01	6.54
E-9	14.20	75.13	4.29	0.09	0.08	0.01	0.34	0.01	5.56
E-11	12.61	78.00	3.88	0.08	0.07	0.01	0.29	0.01	4.94
G-1	34.15	42.25	8.95	0.24	0.21	0.02	0.72	0.02	13.45
G-3	25.89	57.69	5.41	0.17	0.16	0.02	0.56	0.01	10.08
G-5	20.44	66.39	4.44	0.14	0.12	0.01	0.45	0.01	8.00
G-7	17.04	72.00	3.68	0.12	0.10	0.01	0.38	0.01	6.66
G-9	14.60	75.98	3.10	0.10	0.09	0.01	0.34	0.01	5.73
G-11	12.70	79.01	2.73	0.08	0.08	0.01	0.30	0.01	5.01
I-1	35.92	44.37	4.34	0.24	0.22	0.02	0.78	0.02	14.12
I-2	26.40	59.10	3.19	0.15	0.17	0.02	0.58	0.01	10.37
I-3	20.94	67.85	2.52	0.14	0.15	0.01	0.46	0.01	8.11
I-4	17.29	73.25	2.04	0.12	0.11	0.01	0.38	0.01	6.78
I-5	14.87	77.19	1.77	0.11	0.10	0.01	0.33	0.01	5.81
I-6	12.91	79.99	1.55	0.09	0.09	0.01	0.29	0.01	5.06
K-1	37.18	46.00	0.88	0.25	0.21	0.02	0.78	0.02	14.64
K-3	27.14	60.50	0.65	0.19	0.18	0.02	0.58	0.01	10.73
K-5	21.40	68.90	0.52	0.15	0.14	0.01	0.46	0.01	8.41
K-7	17.69	74.30	0.44	0.12	0.13	0.01	0.38	0.01	6.92
K-9	15.02	78.17	0.37	0.10	0.10	0.01	0.33	0.01	5.89
K-11	13.10	80.95	0.33	0.09	0.09	0.01	0.29	0.01	5.13

TABLE II

THE CHEMICAL COMPOSITION OF THE MIXTURES AFTER FIRING

No.	Alumina, Al_2O_3	Silica, SiO_2	Iron oxide, Fe_2O_3	Titanium oxide, TiO_2	Calcium oxide, CaO	Magnesium oxide, MgO	Alkalies, $Na_2O + K_2O$
A-1	35.80	44.18	18.70	0.26	0.24	0.02	0.80
A-3	26.28	59.18	13.55	0.19	0.18	0.02	0.60
A-5	21.25	67.50	10.53	0.14	0.13	0.01	0.44
A-7	17.25	73.40	8.70	0.12	0.11	0.01	0.41
A-9	14.80	77.52	7.40	0.11	0.11	0.01	0.35
A-11	12.97	80.10	6.40	0.10	0.10	0.01	0.31
C-1	36.10	44.65	17.93	0.26	0.24	0.02	0.80
C-3	27.04	60.75	11.23	0.19	0.17	0.02	0.61
C-5	21.25	69.29	8.77	0.10	0.10	0.01	0.48
C-7	17.57	74.62	7.20	0.10	0.09	0.01	0.41
C-9	14.95	78.30	6.20	0.10	0.09	0.01	0.35
C-11	13.12	81.20	5.23	0.07	0.06	0.01	0.31
E-1	38.63	47.64	12.23	0.28	0.25	0.02	0.88
E-3	27.80	62.33	8.80	0.23	0.22	0.02	0.61
E-5	21.77	70.50	6.82	0.21	0.20	0.01	0.48
E-7	17.86	75.75	5.60	0.19	0.18	0.01	0.41
E-9	15.10	79.75	4.50	0.15	0.13	0.01	0.36
E-11	13.28	82.10	4.10	0.10	0.09	0.01	0.31
G-1	39.48	48.85	10.30	0.28	0.24	0.02	0.83
G-3	28.80	64.16	6.03	0.19	0.18	0.02	0.82
G-5	22.30	72.16	4.78	0.15	0.13	0.01	0.49
G-7	18.30	77.00	3.94	0.13	0.11	0.01	0.41
G-9	15.53	80.60	3.29	0.11	0.10	0.01	0.36
G-11	13.41	83.20	2.88	0.09	0.09	0.01	0.32
I-1	41.90	51.59	5.06	0.28	0.26	0.02	0.90
I-3	29.40	66.02	3.56	0.19	0.17	0.02	0.65
I-5	22.75	73.68	2.74	0.16	0.16	0.01	0.50
I-7	18.56	78.60	2.16	0.13	0.12	0.01	0.42
I-9	15.72	81.80	1.88	0.12	0.11	0.01	0.36
I-11	13.62	84.20	1.63	0.10	0.10	0.01	0.36
K-1	43.48	54.00	1.03	0.29	0.27	0.02	0.91
K-3	30.27	67.70	0.73	0.21	0.20	0.02	0.87
K-5	23.41	75.20	0.57	0.16	0.15	0.01	0.50
K-7	19.00	79.84	0.47	0.14	0.13	0.01	0.41
K-9	16.00	83.03	0.39	0.11	0.11	0.01	0.35
K-11	13.80	85.33	0.35	0.10	0.10	0.01	0.31

Experimental Results

The Effect of Varying Salt Glazing Temperatures upon the Glossiness of Salt Glazes

The influence of different salt glazing temperatures upon the smoothness and brightness of salt glazes is shown graphically in Figures 1, 2, 3 and 4. Salt glazing clays at higher temperatures will produce duller glazes on clays containing a high content of iron oxide than when they are salt glazed at low temperatures, see Table III.

TABLE III

THE BRIGHTNESS OF GLAZES OBTAINED ON THE MIXTURES AT DIFFERENT TEMPERATURES

No. of mixture	Cone 02	Cone 3	Cone 7	Cone 10
A-1	Matt	Matt	Matt	Matt
A-3	Matt	Matt	Matt	Matt
A-5	Matt	Matt	Matt	Matt
A-7	Semi Matt	Matt	Matt	Matt
A-9	Semi Matt	Semi Matt	Matt	Matt
A-11	Bright	Semi Matt	Semi Matt	Matt
C-1	Matt	Matt	Matt	Matt
C-3	Matt	Matt	Matt	Matt
C-5	Matt	Matt	Matt	Matt
C-7	Semi Matt	Semi Matt	Matt	Matt
C-9	Bright	Semi Matt	Matt	Matt
C-11	Bright	Bright	Semi Matt	Matt
E-1	Matt	Matt	Matt	Matt
E-3	Matt	Matt	Matt	Matt
E-5	Semi Matt	Matt	Matt	Matt
E-7	Semi Matt	Semi Matt	Matt	Matt
E-9	Bright	Bright	Semi Matt	Matt
E11	Bright	Bright	Semi Matt	Matt
G-1	Matt	Matt	Matt	Matt
G-3	Matt	Matt	Matt	Matt
G-5	Semi Matt	Semi Matt	Matt	Matt
G-7	Bright	Semi Matt	Semi Matt	Matt
G-9	Bright	Bright	Semi Matt	Semi Matt
G-11	Bright	Bright	Bright	Semi Matt
I-1	Matt	Matt	Matt	Matt
I-3	Matt	Matt	Matt	Matt
I-5	Semi Matt	Semi Matt	Semi Matt	Matt
I-7	Bright	Bright	Semi Matt	Semi Matt
I-9	Bright	Bright	Bright	Bright
I-11	Bright	Bright	Bright	Bright
K-1	Matt	Matt	Matt	Matt
K-3	Semi Matt	Semi Matt	Semi Matt	Semi Matt
K-5	Bright	Bright	Bright	Bright
K-7	Bright	Bright	Bright	Bright
K-9	Bright	Bright	Bright	Bright
K-11	Bright	Bright	Bright	Bright

The results can be approximately expressed much simpler by means of the following formula:

$$g_1x_1 + g_2x_2 + g_3x_3 = 100G \qquad (1)$$

x_1, x_2 and x_3 represent the percentages of alumina, silica and iron oxide, respectively, in the clay in terms of calcined weight. g_1 and g_2 represent the gloss factors for alumina and silica, which were found to be -1.00 and $+0.376$, respectively. The value g_3 which represents the gloss factors for iron oxide was found to vary from −2.27 to −7.85 depending upon the salt glazing temperature. This factor was found to be −2.27 at cone 02, −2.923 at cone 3, −4.75 at cone 7, and −7.85 at cone 10, see Figure 5.

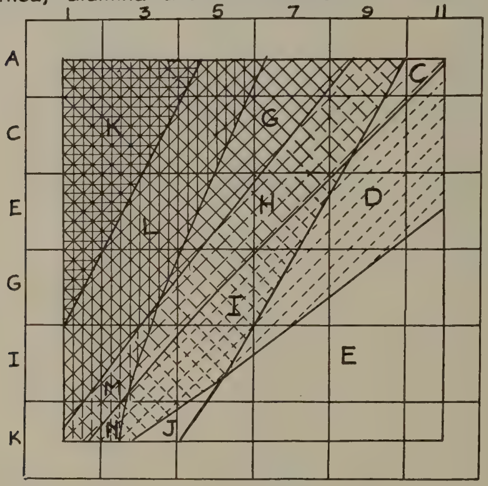
The value of g_2 may also be calculated for different temperatures by means of the following equation in which T is the salt glazing temperature in degrees Centigrade.

$$g_3 = -1.885 - 0.385\ (1.01253)^{(T-1110)} \qquad (2)$$

The observed values for g_3 and those calculated by equation 2 are given below:

Temperature, °C.	Observed value for g_3	Calculated value for g_3
1110	−2.270	−2.270
1190	−2.923	−2.928
1270	−4.750	−4.710
1330	−7.850	−7.851

Figure 1.
The color and gloss of salt glazes obtained at cone 02 on clays of varying silica, alumina and iron oxide contents.



C- Brown Bright.
D-Light Brown Bright.
E-White to Tan Bright.
G-Mahogany Semi Matt.
H-Brown Semi Matt.
I-Light Brown Semi Matt.
J-White to Tan Semi Matt.
K-Dark Brown to Black Matt.
L-Mahogany Matt.
M-Brown Matt.
N-Light Brown Matt.

G in equation 1, represents the gloss factor of the glaze produced with this clay and increases in proportion to the brightness and smoothness of the glaze. When G is greater than 0, the clay will produce a bright glaze provided it is fired under conditions similar to those under which the test pieces were fired.

When G is between −0.1337 and 0, the glazes will be semi matt and when below −0.1337 they will be matt.

The glazes which may be obtained on a clay in which the chief ingredients are silica, alumina, and iron oxide may vary in gloss considerably, depending upon the temperature at which it is salt glazed. The maximum percentages of iron oxide allowable in clays to produce bright and semi matt glazes at different salt glazing temperatures are given below:

Ratio of per cent silica to per cent alumina	Appearance	Cone 02	Cone 3	Cone 7	Cone 10
2	Bright	.. [1]	..	..	..
	Semi Matt	2.23	1.78	1.07	0.64
4	Bright	4.26	3.34	2.08	1.27
	Semi Matt	9.90	7.75	4.84	2.95
6	Bright	7.32	5.79	3.64	2.23
	Semi Matt	12.75	10.10	6.35	3.90

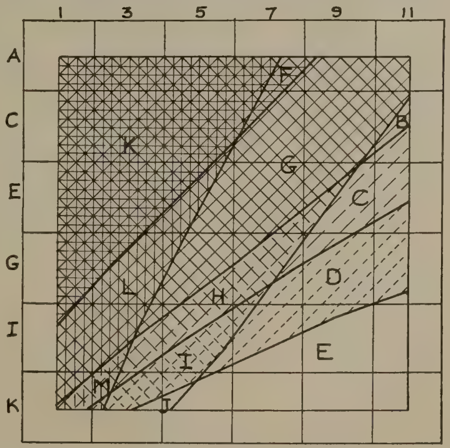
[1] The alumina content is too high to produce bright glaze.

The dulling effect of iron compounds in glazes at high temperatures is probably due to the transition of ferric compounds to ferrous compounds which takes place more readily at high temperatures than at low temperatures.

The Effects of Varying Firing and Salt Glazing Temperatures upon the Color of Salt Glazes

In Figures 1, 2, 3 and 4 and Table IV are shown the effects of different salt glazing temperatures upon the color of salt glazes. This data represents the results obtained in commercial kilns where firing and salt glazing was done under normal conditions. It is possible to obtain darker colors than those obtained in these tests by firing with a reducing kiln atmosphere or lighter colors by firing with an extremely oxidizing atmosphere. These tests apply more closely to clays in which the chief constituents are silica, alumina, and iron oxide, the other ingredients totalling to less than 1 per cent.

Figure 2.
The color and gloss of salt glazes obtained at cone 3 on clays of varying silica, alumina and iron oxide contents.



B- Mahogany Bright.
C- Brown Bright.
D- Light Brown Bright.
E- White to Tan Bright.
F- Dark Brown to Black Semi Matt.
G- Mahogany Semi Matt.
H- Brown Semi Matt.
I- Light Brown Semi Matt.
J- White to Tan Semi Matt.
K- Dark Brown to Black Matt.
L- Mahogany Matt.
M- Brown Matt.

This data shows that salt glazing clays at higher temperatures darken the color of the pipe. With low silica clays the desirable brown and mahogany colors are obtained at cone 02, with clays containing 4.2 to 10.0 per cent iron oxide, at cone 3. These same colors are produced on clays containing 2.7 to 6.2% iron oxide; at cone 7 they are obtained with clays containing 1.7 to 4.0% iron oxide; and at cone 10, they are produced on clays containing 1.3 to 2.9% iron oxide. As the silica content is increased more iron oxide is required to produce the same colors.

The percentages of iron oxide necessary to produce the desirable brown color at different temperatures with clays containing variable amounts of silica and alumina are given below:

Ratio of per cent silica to per cent alumina	Cone 02	Cone 3	Cone 7	Cone 10
2	4.2 to 10.0	2.7 to 6.2	1.7 to 4.0	1.3 to 2.9
4	5.2 to 12.0	3.4 to 7.8	2.2 to 5.0	1.6 to 3.7
6	6.2 to 13.0	4.0 to 8.4	2.6 to 5.4	1.9 to 4.0

TABLE IV

THE COLOR OF GLAZES OBTAINED ON THE MIXTURES AT DIFFERENT TEMPERATURES

No. of mixtures	Cone 02	Cone 3	Cone 7	Cone 10
A-1	Black	Black	Black	Black
A-3	Dark brown	Black	Black	Black
A-5	Mahogany	Black	Black	Black
A-7	Mahogany	Dark brown	Black	Black
A-9	Brown	Mahogany	Black	Black
A-11	Brown	Mahogany	Dark brown	Black
C-1	Black	Black	Black	Black
C-3	Dark brown	Black	Black	Black
C-5	Mahogany	Dark brown	Black	Black
C-7	Mahogany	Mahogany	Black	Black
C-9	Brown	Mahogany	Dark brown	Black
C-11	Light brown	Mahogany	Mahogany	Black
E-1	Dark brown	Black	Black	Black
E-3	Mahogany	Dark brown	Black	Black
E-5	Mahogany	Mahogany	Black	Black
E-7	Brown	Mahogany	Dark brown	Black
E-9	Light brown	Brown	Mahogany	Black
E-11	Light brown	Brown	Mahogany	Dark brown
G-1	Dark brown	Dark brown	Black	Black
G-3	Mahogany	Mahogany	Black	Black
G-5	Brown	Mahogany	Dark brown	Black
G-7	Light brown	Brown	Mahogany	Dark brown
G-9	Tan	Light brown	Mahogany	Mahogany
G-11	Tan	Light brown	Brown	Mahogany
I-1	Mahogany	Mahogany	Black	Black
I-3	Brown	Mahogany	Mahogany	Dark brown
I-5	Light brown	Light brown	Mahogany	Mahogany
I-7	Tan	Light brown	Light brown	Mahogany
I-9	White	Tan	Tan	Brown
I-11	White	Tan	Tan	Brown
K-1	Brown	Brown	Brown	Brown
K-3	Light brown	Light brown	Light brown	Light brown

K-5	Tan	Tan	Tan	Tan
K-7	White	White	White	White
K-9	White	White	White	White
K-11	White	White	White	White

The color of the glazes obtained upon clays, containing varying iron oxide, silica, and alumina contents may be expressed in the following equation in which C is the color factor of the glazes and varies in proportion to the darkness of color. When C is between 0 and 2.0 per cent, the clay will take white to tan glazes; when this falls within 2.0 and 3.5, it will produce light brown colors; when between 3.5 and 4.75 it will produce brown glazes; when between 4.7 and 8.2 it will produce mahogany colors, and when over 8.2 it will produce dark brown to black glazes.

$$c_1x_1 + c_2x_2 + c_3x_3 = 100C \quad (3)$$

x_1, x_2 and x_3 represent the percentages of alumina, silica, and iron oxide, respectively, in the clay in terms of calcined weight. c_1 and c_2 represent the color factors which were found to be +10.30 and −2.65 for alumina and silica, respectively. The color factor for iron oxide, c_3, varies from 68.7 to 244.0 depending upon the salt glazing temperature, see Figure 5.

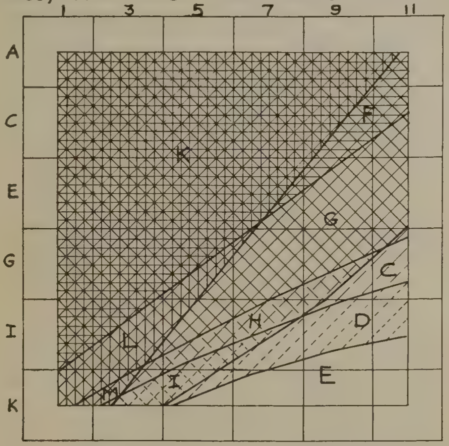


Figure 3.
The color and gloss of salt glazes obtained at cone 7 on clays of varying silica, alumina and iron oxide contents.

C- Brown Bright.
D- Light Brown Bright.
E- White to Tan Bright.
F- Dark Brown to Black Semi Matt.
G- Mahogany Semi Matt.
H- Brown Semi Matt.
I- Light Brown Semi Matt.
K- Dark Brown to Black Matt.
L- Mahogany Matt.
M- Brown Matt.

The value, c_3, may be approximately calculated from the following empirical formula for different temperatures:

$$c_3 = 14.6 + 54.1\,(1.0066)^{(T-1110)} \qquad (4)$$

T is the salt glazing temperature in degrees Centigrade.

c_3 may also be obtained by referring to the curve for iron oxide in Figure 5.

The calculated and the observed values for c_3 are given in the following table:

Temperature, °C.	Observed values for c_3	Calculated values for c_3
1110	68.7	68.7
1190	106.0	106.0
1270	165.0	169.0
1330	244.0	244.0

The darkening effect of iron compounds upon the color of sewer pipe glazes is probably due to the transition of ferric compounds to ferrous compounds which takes place readily at high temperatures. Ferric silicates give red colors to glazes while ferrous silicates as a rule produce black colors.

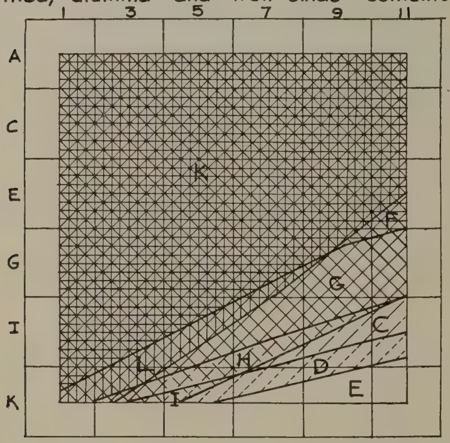
Varying the Salt Glazing Temperatures and Composition of the Body as Means of Improving the Quality of Sewer Pipe Glazes

Clays containing a high iron oxide content should be fired and salt glazed at as low temperatures as possible in order to produce glazes having the best color and smoothness, while clays having a low iron oxide content should be salt glazed at higher temperatures to produce the dark colors.

The writer has previously shown[1] that the brightness of sewer pipe glazes can be increased by adding fine silica to a clay.

Figure 4

The color and gloss of salt glazes obtained at cone 10 on clays of varying silica, alumina and iron oxide contents.



C-Brown Bright.
D-Light Brown Bright.
E-White to Tan Bright.
F-Dark Brown to Black Semi Matt.
G-Mahogany Semi Matt.
H-Brown Semi Matt.
I-Light Brown Semi Matt.
K-Dark Brown to Black Matt.
L-Mahogany Matt.

The results of this work indicate that decreasing the iron oxide content will also greatly improve the brightness and smoothness of salt glazes. For example reducing the iron oxide content 1.00% is equivalent in its effect upon the brightness of glazes to the addition of 6.1% silica when glazed at cone 02, to the addition of 7.8% silica when glazed at cone 3, to the addition of 12.6% silica when glazed at cone 7, and to the addition of 20.8% silica when glazed at cone 10.

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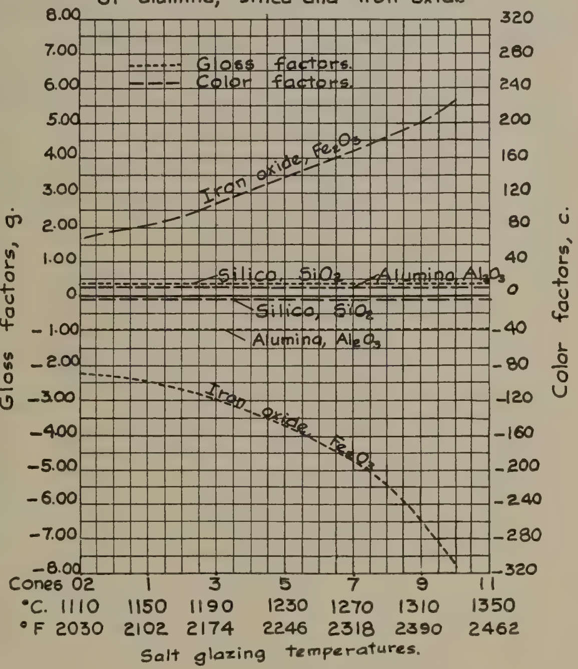
[1] The effect of variable alumina, silica and iron oxide in clays on some properties of salt glazes, *loc. cit.*

Decreasing the alumina content one per cent is equivalent to increasing the silica content 2.7%. This relation does not change much with an increase in temperature as is the case with iron oxide, but remains practically constant for temperatures between cone 02 and cone 10.

Summary and Conclusions

Since these tests were conducted in commercial kilns, the results apply fairly accurately when the ware is fired and salt glazed in commercial kilns under normal conditions. These results also apply more particularly to clays composed chiefly of alumina, silica, and iron oxide, the other impurities totalling to less than 1.00%. If the kiln is fired extremely reducing the glazes obtained would be similar to those obtained at high temperatures. If fired strongly oxidizing the results would approach those obtained at lower temperatures.

Figure 5.
The influence of different salt glazing temperatures upon the gloss and color factors of alumina, silica and iron oxide



1. Increasing the salt glazing temperatures causes those clays containing iron oxide to take duller glazes. The effects of varying salt glazing temperatures upon the brightness of salt glazes may be determined by calculating the gloss factor G in the following equation. When G is greater than 0, the glaze will be bright, when between −0.1337 and 0 it will be semi matt and when below −0.1337 it will be matt.

$$-1.00x_1 + 0.376x_2 - (1.885 + 0.385\ (1.01253)^{(T-1110)})x_3 = 100G$$

2. Increasing the salt glazing temperatures darkens the glazes obtained on clays containing iron oxide.

The color of the glazes may be obtained by calculating C in the following equation. C varies in proportion with the darkness of the color.

If between 0 and 2.00 white to tan colors will be produced; if between 2.00 and 3.5 light brown colors will be obtained; if between 3.5 and 4.75 brown colors will be produced; if between 4.75 and 8.2 mahogany colors will be obtained; and if above 8.2 dark brown to black colors will be obtained.

$$10.3x_1 - 2.65x_2 + (14.6 + 54.1\ (1.0066)^{(T-1110)})x_3 = 100C$$

3. Clays containing a high iron oxide content should be salt glazed at low temperatures, while clays having a low iron oxide content should be salt glazed at high temperatures to produce desirable glazes.

4. Decreasing the iron oxide contents will greatly improve the brightness of the salt glaze. This effect will be greater at higher temperatures than at low temperatures.

5. Decreasing the alumina content will improve the brightness of the salt glaze. This effect is about the same at all temperatures.

6. High alumina clays with a certain percentage of iron oxide produce darker colored glazes than high silica clays with the same percentage of iron oxide.

In conclusion the writer wishes to acknowledge his indebtedness to Dr. E. W. Tillotson for helpful advice during the progress of this work.

SOME UNAVOIDABLE HEAT LOSSES IN THE USE OF PERIODIC SYSTEMS[1]

By Robert H. Armstrong

ABSTRACT

This paper deals with an approximation of the heat lost: (1) In cooling ware from drier temperature to air temperature and the subsequent reheating. (2) In getting rid of moisture absorbed while ware is cooling and being set in kilns. (3) In a waste heat drier system. All heat values are summed up both for one single burn and over a year's time in tons of average coal representing these losses.

Introduction

The best kiln ever built lacks in efficiency. There are losses of heat in periodic kilns due to heating up of the cold kiln and the cooling of the hot one. In this article three different losses are approximated. Minor they may be, nevertheless they are important.

1. Loss due to cooling the ware from drier to air temperature and the subsequent reheating. 2. Loss due to moisture absorbed while the ware is cooling and being set in the kilns. 3. Loss of heat in a waste heat drier system.

To state in final terms of tons of coal wasted we shall use 12,546 B.t.u. per pound as the heat value of the average bituminous coal. This equals 25,092,000 B.t.u. per ton.

Due to Cooling from Drier Temperature

Coming from the drier at 250°F the brick are cooled to air temperature in order to be handled by the setters. This cooling loss is small but amounts to considerable in a year. Specific heat of the mass: $\left(\frac{H}{m(t_2-t_1)}\right)$ from which we get H equals $sm(t_2-t_1)$, where H is the heat developed in calories, m is the mass in grams, s the specific heat, and t the temperatures in °C. The "Clay Products Cyclopedia" gives the specific heat of clay as 0.23. The temperatures are 121° and 21°C. The average dry weight of a brick was found to be 2825 grams. With these values $H = 0.23 \times 2825 \times 100$ or 64,975 calories per brick lost in cooling. Since 252 gram-calories equal 1 B.t.u. this loss of heat is equivalent to 257.8 B.t.u. per brick. For each kiln of 132,000 bricks set, there is lost from this cause alone $132{,}000 \times 257.8$ B.t.u., or 34,029,600 B.t.u., a loss of 1.36 tons of coal on each burn.

Loss Due to Moisture Absorbed

Clay absorbs moisture as soon as it is exposed to the atmosphere and cooled down to air temperature. In order to determine just how much moisture a brick gains while cooling and being set, two lots of ten brick each were accurately weighed as they came from the drier, then boxed in with other brick to get setting conditions and reweighed at intervals. The relative humidity and temperature of the air were taken at each weighing. Table I gives the results of one of these experiments. All weights are given in grams.

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[1] Presented at the Atlantic City Meeting, Feb., 1924 (Heavy Clay Products Division).

TABLE I

Brick No.	Dry weight	At 24 hrs.		At 48 hrs.		At 72 hours	
		Weight	Gain	Weight	Gain	Weight	Gain
1	2706	2712	6	2714	8	2716	10
2	2725	2730	5	2731	6	2734	9
3	2746	2753	7	2755	9	2756	10
4	2742	2748	6	2750	8	2753	11
5	2778	2786	8	2787	9	2789	11
6	2747	2754	7	2754	7	2756	9
7	2760	2765	5	2766	6	2770	10
8	2788	2797	9	2797	9	2800	12
9	2812	2819	7	2822	10	2824	12
10	2849	2856	7	2857	8	2859	10
Average Gain		6.7 g.		8.0 g.		10.4 g.	
Per cent Gain		0.24%		0.29%		0.37%	

	Start	At 24 hrs.	At 48 hrs.	At 72 hrs.
Rel. Hum.	87	60	64	67
Temp. Air	52	48	37	50

Average dry weight of a brick 2773 grams or 6.1 pounds.

Our time for setting a kiln averages three days. To get the moisture gained during these thirty-six hours we take the mean between the twenty-four and forty-eight hour gains. This is 7.4 grams. With 132,000 bricks to a kiln this means 976,800 grams or 2152 pounds of water are absorbed. To evaporate this moisture at 70°F requires 1052 B.t.u. per pound or a total of 2,263,904 B.t.u. for each kiln or 0.09 tons of coal.

Loss of Heat in a Waste Heat Drier System

A kiln of brick just burned off contains heat energy which is largely wasted. The loss through radiation is immense. For nearly twenty-four hours after the conclusion of the burn, the stack dampers are open to rid the kiln of gases. This wastes considerable heat which if used for drying would scum the brick. The kiln walls, crown, flues and stacks contain a lot of usable heat. But in calculating only the actual drying value of the heat stored in 132,000 bricks at 960°C the following data are available.

The brick burned weighs 5.5 pounds or 2495 grams. One brick cooling from 960° to 21°C releases $.23 \times 2495$ grams $(960° - 21°)$ or 538,845 calories or 2138 B.t.u. One hundred and thirty-two thousand bricks release 282,216,000 B.t.u., an equivalent of 11.24 tons of coal.

A wet brick weighing 3082 grams has a drying loss of 257 grams of water. The evaporation of 257 grams or 0.566 pounds of water at 21 °C requires .566 × 1052 B.t.u. or 595 B.t.u. The heating up of a brick to drier temperature we found before to require 258 B.t.u. The total heat requirement per brick in the drier is 258 plus 595 or 853 B.t.u. A kiln of hot brick should then be capable of drying 330,850 bricks.

With eleven kilns a month available no kiln need be used for the drier more than three days. Even at this our drier temperature sometimes falls to 100 °F. If the drier is doing its best 45% of 11.24 tons or 5.06 tons of coal value are wasted per kiln unit.

If the sulphur compounds in the gases of the cooling kiln could be rendered inocuous as scum producer on the wet brick, it would make possible the use of much of this heat now wasted. Unfortunately, only the sulphates which do not decompose at this temperature are sodium and zinc but they are white. Such sulphates as manganous and ferrous sulphates which would add to the color of the ware will decompose. Cobaltous and vanadium sulphates could be formed at somewhat lower temperatures but the cost would be prohibitive.

Conclusions

We have found by very fair approximation that from these three minor sources alone, for each kiln unit of brick the losses are from:

		Tons
1.	Cooling brick from drier..............	1.36
2.	Moisture absorbed while cooling.......	.09
3.	Heat lost in drier system at its best....	5.06
	Kiln total	6.51

One hundred and thirty-two kilns of brick are burned off on the average in a year. The losses give in a year:

1	179.52 tons
2	11.88
3	667.92
Yearly total	859.32

In other words twelve and a quarter large cars of coal are bought in a year to produce this wasted heat, enough to have burned thirteen or fourteen more kilns.

Fiske & Co., Inc.
Watsontown, Pa.

Discussion

Mr. Thwing: In allowing it to cool down to room temperature and then starting over again and heating it up to burning do you not lose that heat only once?

Mr. Armstrong: If you are using a continuous kiln your brick runs straight from the drier into the continuous kiln and you have that much heat in the brick going into the tunnel kiln which does not have to be regained whereas if it was cooled down that many degrees when it went into the kiln it would have to be reheated and the same amount of heat would have to be put back in.

Mr. Armstrong:[1] It does not make such a great change in the net loss since it only halves a small loss. Concerning the inability of what heat we have available from our kilns being sufficient for drying the brick at all times, I would say that this is due to two main causes. (1) The inability to reserve the heat when not needed for future use when no hot kiln is available. (2) The lack of flexibility in our drier equipment which is able to take care of perfect drying only when the air enters and leaves at certain temperatures and at a certain humidity. As the drier heat falls we have no way of proportionately increasing the speed of the air through the drier and no control over humidity. The nearest approach to perfection, that I have seen, of a waste heat drier is on a plant where all the kiln gases during both burning and cooling are pulled through the drier in 10-inch cast iron pipes by means of a fan and regulated by a damper which shunts any part of this heat out of an outside stack. In any such drying system the plant production must be nearly constant to insure proper drying at all times. In the latter system one great drawback is that the pipes become scaled with sulphur and lime compounds and this must be removed with steam injection.

Mr. Jackson: Mr. Armstrong mentioned casually about ferrous sulphate being used as a possible source of taking up sulphur. In the course of laboratory experiments I found that ferrous sulphate is decomposed in air. I have mixed ferrous sulphate with a pure Georgia clay and it decomposed beginning at around 500°C. It decomposes particularly in a neutral or reducing atmosphere. The decomposition is pretty nearly complete before 800°C is reached. Strangely enough if you heat a mixture of ferrous sulphate and clay in an atmosphere of pure oxygen, heating it up to practically finishing temperature of the kiln, you only get 29% of the sulphur given off.

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[1] Recd. April, 1924.

THE OXIDATION OF CERAMIC WARES DURING FIRING.—III. THE BEHAVIOR OF CALCIUM COMPOUNDS IN CLAYS[1]

By Frederick G. Jackson[2]

ABSTRACT

Previous theories on the formation and decomposition of calcium sulphate as kiln scum are confirmed. Quantitative analyses on the effect of definite heat treatments put the subject on a more definite basis.

Introduction

Calcium compounds occur in practically all clays and may be present in amounts varying from a fraction up to 30%[3] in commercial clays. The two most common compounds of calcium existing with clay are the carbonate (limestone) and the sulphate (gypsum).

Gypsum is slightly soluble in water, about one part in 500, and consequently may be deposited with a clay by evaporation or washed out by a natural lixiviation. It may be absent from the clay, but present in the pug water. Many scumming troubles have been solved by a change to "soft" water. When the ware is dried, the water evaporating deposits white crystals on the surface of the ware producing the familiar drier scum.

A similar scum, however, can be formed in a kiln in the absence of calcium sulphate in the dried ware. An explanation of this is the purpose of this paper.[4]

Calcium Sulphate Scumming in Kiln

Conditions may be such that calcium sulphate is formed in the kiln from the carbonate. The necessary factors are calcium carbonate, sulphur trioxide, and plenty of water to dissolve it.

The drying can never be complete even for the mechanically combined water, and there is up to 10% of chemically combined water, which is only liberated around 400°C. The top of the kiln heats more rapidly than the bottom. If the draft is not strong the water from the top courses will accumulate in the lower courses and will persist until the top courses get to a dull red heat. At this stage kiln scum is inevitable if limestone is present, due to conversion of the calcium carbonate to calcium sulphate by the sulphur trioxide from the coal gases.

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[1] Published by permission of the Director, U. S. Bureau of Mines.

[2] Associate Chemist, Columbus Station, U. S. Bureau of Mines.

[3] See Seger, "Collected Writings," **1**, 435.

[4] For a popular treatment of this subject without quantitative data, see a series of papers by Ellis Lovejoy in *The Clayworker* for 1906–7. These have been combined in pamphlet form under the title "Scumming and Efflorescence" and published by F. J. Heer, Columbus, Ohio.

Cause of Kiln Scum A laboratory experiment has shown this very clearly. Two bars were made of 14 parts by weight of plastic kaolin[1] and one part of calcium carbonate; also one bar of 14 parts Bedford shale and one of calcium carbonate. One of the kaolin bars was thoroughly dried at 110°C. One kaolin bar and the bar of shale were in a plastic state when all three were put into a glass tube. This tube was connected, through a drying tube, with a combustion furnace. In the combustion tube was a bar of clay containing five grams of $Fe_2(SO_4)_3$. This was heated, evolving SO_2 and SO_3. Gentle suction drew these gases first through the drying tube, then over the dry kaolin bar and then over the wet bars. The bars all had, therefore, an equal chance to absorb sulphur gases. Each bar was then extracted by boiling with successive lots of 500 cc. of distilled water until the filtered extract gave no test for sulphate. They showed the following contents of sulphur trioxide. The equivalent amount of calcium carbonate is also given:

	SO_3 gms.	Equivalent $CaCO_3$%
Pure kaolin dry.........	0.0170	2.12
Pure kaolin wet.........	0.0940	11.76
Bedford shale wet.......	0.0750	9.96

All tests showed the absence of calcium sulphite and sulphide.

This shows that when ware is properly dry there will be little sulphate formation from conversion of calcium carbonate during watersmoking. If the ware is wet, exactly similar conditions will give 10–12% conversion.

Elimination of Kiln Scum That calcium sulphate once formed in ware can be removed is known.[2] In an oxidizing atmosphere, it decomposes only at very high temperatures, but under reducing conditions, it is more easily broken down. A. E. Williams[3] made good black flashed brick from scummy and poor flashing clays by spraying the surface with $FeCl_3$ solution as the clay column came through the die.

Williams also experimented[4] on the reduction of calcium sulphate. With a mixture of 20% gypsum and 80% clay heated in a combustion tube in an atmosphere of pure CO, for two hours at 800°C, he found complete reduction; also with an atmosphere of 44% CO_2, 35% CO, and 2% O_2. With the latter atmosphere for two hours at 750°, he found only slight reduction, and at 700° for two hours no reduction; for three hours a slight reduction.

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[1] For analysis of this see *Jour. Amer. Ceram. Soc.*, **7** [4], 224(1924).

[2] See Seger, "Collected Writings," **1**, 148; also Garve, *Trans. Amer. Ceram. Soc.*, **17**, 600(1915).

[3] *Trans. Amer. Ceram. Soc.*, **17**, 764(1915).

[4] *Ibid.*, **18**, 271(1916).

We have investigated this subject from a quantitative standpoint. A number of bars were prepared of 15 grams of plastic kaolin and one gram of celenite ($CaSO_4.2H_2O$) ground intimately together, tempered with distilled water, molded by hand, and dried at 110°. A bar was then put into a combustion tube, heated to the desired temperature and held for an hour with natural gas passing over it. The furnace was then thoroughly cooled with the gas still passing. When cold, the bar was removed and ground fine. It was then extracted by boiling with successive lots of 500 cc. each of distilled water, boiling each for half an hour. The filtrates were analyzed[1] for SO_3 and SO_2 until extraction was complete.

Evidence pointed to the probability of there being much more sulphide than sulphite. However, sulphide and sulphite would behave alike in reoxidizing to sulphate and they are, therefore, combined in the analysis.[2]

Temperature	700°C	750°C	800°C	850°C
$CaSO_4$ remaining, %	85.22	31.04	9.92	4.20
$CaSO_3$ or CaS formed, %	14.07	46.87	39.14	39.10
CaO by difference, %	0.71	22.09	50.94	56.70

From these results it would appear possible to remove a large amount of drier scum or kiln white from scummed ware by maintaining a reducing condition in the neighborhood of 800–850°, and following this by oxidation.

CERAMIC EXPERIMENT STATION
U. S. BUREAU OF MINES
COLUMBUS, OHIO

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[1] For a description of the method of analysis, see *Jour. Amer. Ceram. Soc.*, **7** [3], 169(1924).

[2] The method of this combined analysis is discussed in *Jour. Amer. Ceram. Soc.*, **7**, 228(1924).

PLASTICITY AS A MEANS FOR CONTROL OF PROPERTIES[1]

By Eugene C. Bingham

Perhaps in no field is the property of plasticity more important than in the ceramic industry and the nature of plasticity has been better understood in this industry than in any other. But the early efforts to measure it directly seem to have failed very largely for the measurements of plasticity given in the literature have been largely indirect in nature based on shrinkage on drying or burning, tensile strength or adsorption of malachite green, etc. The records of the flow of clay slip were very scanty presumably due to the difficulty in obtaining data which were reliable indications of the property.

There is every advantage in having a variety of indirect methods for measuring the property in question, but indirect methods have their greatest value only when direct methods are available for the exact measurement of the property. This principle is particularly well illustrated in the case of plasticity. It is now known that the viscosity of a colloid, such as clay slip, is not a constant but varies with the shearing stress applied, so viscosity measurements as such mean very little. If the rate of deformation is plotted against the shearing stress a pure liquid gives a linear curve passing through the origin as *OA* in Fig. 1. But a plastic substance gives a curve *BC*. A certain shearing stress *OB*, the yield value, is required to start the flow but after the flow is started the increase in shearing stress increases the flow just as in true liquids, the result being that a plastic material may yield little if any as pressure is first applied but when a certain pressure is exceeded it yields rapidly. The property analogous to the fluidity of liquids is called *mobility* and the property analogous to viscosity is probably *consistency*.

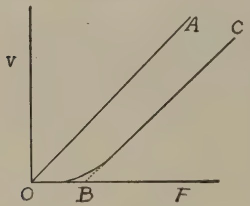

Fig. 1.

Just as metals below their elastic limit are known to yield very slightly, so plastic materials in general yield somewhat before the yield point is reached. Thus the curve *BC* bends off toward the origin at low shearing stresses.

This much seems to be established by the very incomplete researches which have been carried out thus far on the subject of viscous and plastic flow. And this is enough to show that no single property such as tensile strength, adsorption of dye or shrinkage can possibly be a measure of plasticity, for plasticity is a complex property made of two properties which are mutually independent. One of these properties may be an exact measure of the yield value *or* of the mobility but not of *both* at the same time.

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[1] Presented at the Atlantic City Meeting, Feb., 1924 (Whitewares Division).

We arrive, therefore, at the conclusion that in order to control the plasticity of clay we must obtain knowledge of the factors which affect the yield value and mobility.

Other properties which depend on the flow of solids such as hardness, malleability, ductility are also complex properties which probably may be quantitatively defined and measured in terms of yield value, mobility and so forth. It can even be shown that in emulsion colloids the terms melting-point and solubility as well as viscosity are vague in their meaning, but that through a knowledge of plastic flow it is possible to give these properties a meaning analogous at least to that which they have in classical chemistry. It would be out of place here to go into details of that subject.

It may, however, be not inappropriate to outline here how control properties of value may be expected to result even in colloidal suspensions such as clay or paint. Paint has offered an attractive subject for investigation because the dispersion medium may be made non-volatile. It has been found that the mobility rapidly lowers as the concentration increases and in a linear manner so that if one knows the fluidity of the medium and the mobility of one mixture, it would be possible to calculate the mobility of any mixture whatever. There is a definite mixture at which the mobility would become zero and this is evidently connected with the close packing of the clay or paint.

The yield value-concentration curve is also linear over a certain range, the yield value increasing rapidly as the concentration is increased. By extrapolation there is a certain concentration at which the yield value would be expected to be zero. This concentration is presumably dependent upon the size of the particles but particularly upon the adhesion between the particles. Thus a paint ground in mineral oil showed a loss of 81% in its yield value of 1090 when only 0.2 per cent of oleic acid was added, without affecting the mobility. The addition of very small amounts of various classes of substances are of very great importance. Thus the addition of a soap (aluminum stearate) to a paint was found to decrease the mobility only slightly (12%) whereas the yield value was raised nearly 800%. As another proof of the great effect of small additions, 0.5% of moisture raised the yield value of a paint 3700%. In a similar way we might expect small quantities of an oil or colloid to greatly affect the yield value of a clay slip. It has already been shown that the effect of small amounts of acid exert a prodigious effect on the yield value.

The effect of temperature is to raise the mobility in the same ratio as the temperature raises the fluidity of the medium. But the temperature has no effect on the yield value. It is inferred that other causes which brought about an increase in the fluidity of the medium would also increase the mobility without necessarily affecting the yield value.

With such prodigious effects upon first the yield value and then upon the mobility or sometimes on both, we may safely assume that a knowledge of these properties will permit better control in the ceramic industry and it will disclose the means for obtaining properties in clay which are desired but which are now somewhat mysterious. Given two new properties of a fundamental nature which can be quantitatively measured it seems useless to ask whether they may be of use. What is needed is much more work carried out in close coöperation with the industries.

The university offers a suitable place for the investigation of the methods of measurement, of the basic laws and theories of flow. The industries have an enormous fund of practical knowledge of what is wanted even where the reason why cannot be assigned. The happy union of these two forces ought to result in the progress of American industry and in the broadening of the theoretical foundation of the Science of Colloid Chemistry.

LAFAYETTE COLLEGE
EASTON, PA.

Discussion

DR. SCHRAMM: As I understand it, Dr. Bingham's work on plasticity has been on slips. He has referred to paint slips and to clay slips. If he would translate the work into the determination on the properties of clay in the plastic condition so that the properties which determine the actual plasticity of clay as it is worked, may be determined, the method would be of a real practical value to the potters.

DR. BINGHAM: Our first work on clay slips was in 1916. As I understand you, what is really wanted is a correlation between the properties as we measure them in the clay slip which has a high percentage of water with the properties which are in the plastic clay as it is actually cast.

DR. SCHRAMM: That is right.

DR. BINGHAM: It seems to me that there is a gap right there, which needs to be filled in by further investigation.

DR. SCHRAMM: Is there a possibility of making these measurements in the plastic clay directly?

DR. BINGHAM: It seems to me that is where it *should* be done and there ought not to be any experimental difficulty unless the particles are of an extremely great size so that they would clog up the tubes that are used.

It is advantageous, in measuring plasticity, to use small tubes of considerable length. We have had very good results in working with materials like the dental impression compounds which are used to get the impression of the mouth. They contain varnish gum, stearic acid and perhaps talc mixed together, and the amount of flow which one gets through the plastometer with any degree of pressure is very small, and yet it gives very interesting and helpful results.

MR. MCAFEE: It seems to be impossible to base calculations exactly on the clay taken in any unit. For instance the moisture content will vary considerably between the pieces lying side by side in the clay bin. Methods of taking samples tend to give average results but this is not exact. It also does not seem possible to determine by exact scientific means whether or not a clay slip is just right for casting. Determinations of viscosity and specific gravity do not tell the whole story. Different samples of the same clay shipment give different results when used in the same formula.

PROF. SHAW: I have been trying to decide whether we were discussing here the subject of viscosity or plasticity, and whether there is a distinction. I have not thought plasticity and viscosity were the same. Definitely, what is plasticity?

DR. BINGHAM: To my mind plasticity always refers to a substance which can be readily molded or shaped under a convenient shearing stress, but which will hold its shape when the shearing stress is removed. Pitch is not a plastic solid, because it does not hold its shape. Quartz is not plastic either under ordinary conditions, but for a different reason, *viz.*, because it cannot be molded. There are then two distinct properties involved in the notion of plasticity. The one is the shearing stress required to continuously deform the material which is called the yield value; the second, dependent upon the amount of deformation in a unit cube of the material when the yield value has been exceeded by a definite amount, which is called the mobility.

The reason why a single property, *viz.*, the viscosity, will define the flow properties of a fluid whereas two properties—yield value and mobility—are required to define the plasticity of a solid can best be understood by the use of simple diagram, Fig. 1. It is seen that the volume of flow in a viscous liquid varies directly as the shearing stress, so that deformation takes place at any shearing stress no matter how small and the fluidity is fully determined by one observation. On the other hand, in plastic solids continuous deformation does not take place except when the shearing stress exceeds the yield value f and two determinations are necessary in order to determine the flow characteristics of the material.

DR. SCHRAMM: Could you say that one substance had greater plasticity than another?

DR. BINGHAM: It would be strictly incorrect to speak of one substance as having greater plasticity than another unless it is tacitly assumed that one or the other of the two independent variables is kept constant. For example, it appears that in making up paints the effort of the manufacturer is to keep constant that property which we know as yield value. We can see why this is so, because every paint should have sufficient yield value to remain in place on the surface to which it is applied, but it should not consume an unnecessary amount of energy in the process of application. If then all paints of painting consistency have the same yield value, it would be natural to speak of those paints which have the highest mobilities as the most plastic. Conversely, if in some industries the material used is always made up to a fixed mobility, we can imagine their referring to those substances which have the highest yield values as the most plastic. But whenever plasticity is to be stated quantitatively, it should be done in terms of yield value and mobility. Good plasticity seems to be dependent upon a high yield value and a high mobility.

Dr. Schramm: It is very hard to avoid talking about plasticity. We are constantly using the term to indicate what we might call the working properties in clays. If we are to be deprived of the word plasticity, somebody will have to give us another one.

Dr. Bingham: I think the term plasticity should retain its loose meaning. Ceramists state that a certain clay has good plasticity but they do not mean the same thing that metallurgists mean when stating that zinc is plastic. Still different ideas of plasticity are in mind when one is handling rubber, lime, or nitrocellulose. Each industry needs a certain combination of yield value, mobility and perhaps certain other properties such as elasticity. We can speak perhaps of an *optimum* plasticity for each industry or industrial operation when the yield value and mobility are within certain limits.

Dr. Schramm: Might it not be possible to determine a single factor which would describe the workability of clay without dissecting it in this way?

Dr. Bingham: We can state that a given material has a satisfactory plasticity or workability, but we apparently cannot avoid having to deal with at least two independent variables. Even the painter in his test of plasticity does two things which may test the two variables in question. He stirs the paint carefully observing the resistance to the paddle, which apparently gives an indication of the mobility. He then lifts the paddle up and notices how the paint streams from the paddle and from this we may assume that he gathers some idea of the yield value. It does not seem to me likely that we shall be able to represent the plasticity by any complex factor such as the product of the yield value times the mobility. The reason for this is that the yield value must lie within certain prescribed limits and any passage of these limits in either direction cannot be made up except in a limited degree by adjusting the mobility. I think that it will be readily believed that many clays may be given a prescribed yield value or mobility, by the addition of water in varying quantities, but both of these properties cannot be adjusted at a predetermined value at the same time, so we have plastic and non-plastic clays.

Question: How is the shearing stress applied?

Dr. Bingham: There are a number of ways in which this may be done. With very soft solids we have found it most convenient to force the material through capillary tubes under a measured pressure. The material flowing from the capillary in a given time is then measured in a variety of ways.

Prof. Shaw: Professor Orton distinguished between the plasticity of an asphalt and a material of the character of clay. As I remember it, he termed the plasticity of an asphalt as pseudo-plasticity as distinguished from that of a clay which is normal plasticity. The basis of his distinction being that the plasticity of the asphalt results from mixing a non-plastic powder with a *viscous* liquid, while the plasticity of the clay is characteristic of the powder itself.

Many different methods have been proposed by members of this Society for measuring viscosity. The viscosimeter which measures the quantity of material which flows through a capillary tube is an exact duplicate of what has been described here, except that with that instrument your pressure is simply gravity. Here you are doing precisely the same thing, only you have a high viscosity and are compelled to use a higher pressure to force it through there.

In order to avoid that, Bleininger and a little later, I, myself devised a little different type of viscosimeter in which we used a larger tube. We still used the gravity pressure and measured the viscosity of our material by measuring the quantity of material which flowed in a given time.

In the viscosimeter which I devised, in testing the viscosity of enamels which would not flow through a small capillary tube, I had two tubes—a single cylinder with a $^5/_{32}$-inch tube on one side and a $^3/_{32}$-inch tube on the other, both opening into the same cylinder. I let the material flow through both tubes at the same time, measuring the quantity which flowed through each of the tubes.

We are still dealing with viscosity. We are not dealing with *plasticity*, but rather with simply one of the factors which influences plasticity.

Emley has devised a plasticimeter which he contends measures the plasticity of clay, but as I see it what he does is the same thing as has been done here—he measures the resistance of the clay to the flow. There are a number of different factors which enter here. The friction between the tubes and the material is one factor, and the cohesion between the particles themselves is another factor. There is a complication there which influences the measure of the result and which no instrument yet devised has been able to eliminate. It is a well-known fact that clays of high viscosity are not necessarily highly plastic. On the other hand some mixtures do exhibit plasticity in direct proportion to their viscosity.

I have simply gone into this to repeat what I said awhile ago that this term plasticity covers a number of things in the mind of the ceramic man, and we do not know what we are talking about when we use the term plasticity. The term is described in our ceramic writings as being that property of clay which makes it capable of being molded and of retaining its form until it is changed by the application of some exterior force. That is a definition which has sufficed to date for us, but it is quite meaningless and all efforts spent on trying to reduce it to concrete terms are worthy of commendation. This work of Dr. Bingham's surely falls into that category and I am sure we all wish him success in the pursuit of the subject.

A MEMBER: Dr. J. W. Mellor[1] describes a method of determining the two factors of plasticity on plastic clay. A sphere of clay is compressed by the application of a gradually increasing load until cracks develop. The amount of movement gives the deformability (corresponding to Dr. Bingham's mobility) and the load divided by the distance moved gives the resistance (corresponding to the yield value). A plasticity number is expressed as the product of the two, although Mellor recognizes a qualitative difference in clays according to the magnitude of the two factors. It would appear that the method described by Mellor is correct in principle but experimentally uncertain as the small spheres (only 2 cm. in diameter) are not easy to make. With improvement in technique this method should give a satisfactory basis on which to measure the working qualities of clay.

PROF. WATTS: To me "plasticity" is a combination of viscosity, lubrication value and bonding strength. But I believe that the general opinion holds that the peculiar and specific properties of ball clays are combined in two particular properties, greasiness or lubrication, and stickiness or bonding strength. If every man who has used ball clay would carefully analyze the way ball clay acts when he incorporates it in his body, he will recognize the fact that he is trying to acquire those two properties, greasiness or lubrication and stickiness or bonding strength. In this way, the mass containing ball clay is caused to mold with increased smoothness and the strength in the plastic state and the drying state are both increased.

However, in order to be able to do anything with these values, I have found that it has been necessary to dilute the ball clays, but I have not been satisfied with dilution of ball clays with water, and am now attempting to dilute them with a solid material, using finely pulverized flint in order to reduce the evidence of these properties to a sufficient degree so that I can get some value expression.

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[1] *Trans. Eng. Ceram. Soc.*, **21**, 91–103(1921-2).

A GRAPHICAL CHART FOR DETERMINING EXCESS AIR IN THE COMBUSTION OF PRODUCER GAS[1]

By Gordon M. Peltz

ABSTRACT

This paper presents a mathematical analysis of the combustion of the principal components of producer gas. Formulae are obtained for determining the theoretically right proportions of air to gas for any analysis of producer gas and the theoretical volume of waste gases which should result from this combustion. In addition, a formula is determined by which the percentage of excess air can be obtained when the analysis of the gas and the percentage of CO_2 in the products of combustion are known. These formulae are presented in a chart form which eliminates the necessity for mathematical calculations.

The purpose of this paper is to present a calculating chart[2] by which it is possible to determine the percentage of excess air existing in any producer gas fired furnace when the analysis of the gas and the percentage of CO_2 in the products of combustion are known.

Excess air is a very important factor, not only from the standpoint of fuel economy, but also in cases where the nature of the furnace atmosphere has an effect upon the operation involved. In spite of this, furnace operators rarely make determinations of the excess air, due largely to reluctance to take the time and trouble to make the necessary calculations as a regular daily routine. The desire to make a daily study of this question in a practical way led the writer to reduce the whole calculation to chart form.

This chart has saved valuable time and has made practical a daily study of the excess air conditions in furnaces. Hoping that the same may prove valuable to others, the chart and its derivation are herewith presented.

For furnaces using an unchanging fuel such as natural gas, coal or oil it is a comparatively simple thing to calculate the excess air represented by any given percentage of CO_2 in the flue gas. Having once made such a calculation a table can be made by which the percentage of excess air could be read directly from the percentage of CO_2. However, in considering producer-gas furnaces it is necessary to take into consideration the continually varying composition of the gas being used. The combustion of producer gas is in fact a two-stage combustion of coal but when so considered there is no way of determining the relative merits of the producer operation and the furnace operation. To properly judge the combustion of the furnace alone, apart from the producer supplying it, it is necessary to analyze the gas received by the furnace and the products of combustion delivered by it to the stack.

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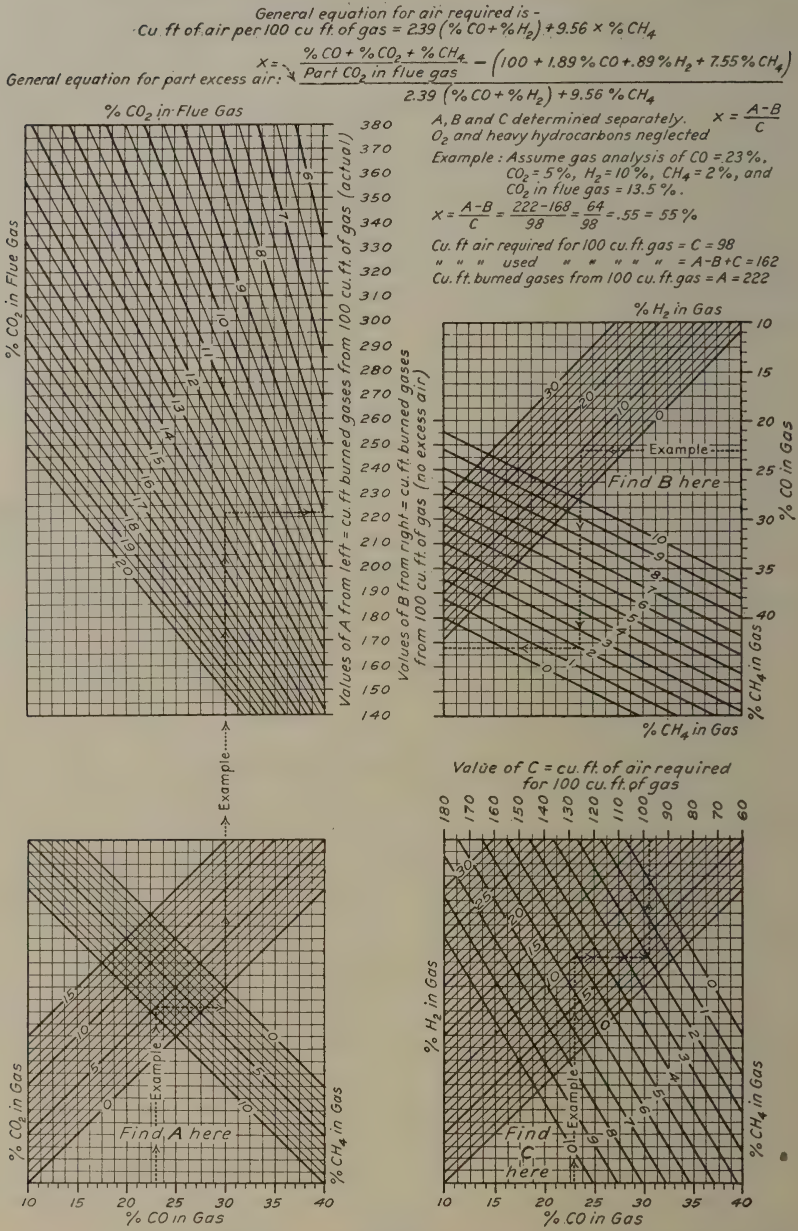
[1] Presented at the Atlantic City Meeting, Feb., 1924 (Glass Division).

[2] Full size copies of this chart can be obtained by anybody by communicating with the author ℅ Corning Glass Works, Corning, N. Y.



General equation for air required is -

Cu. ft of air per 100 cu ft. of gas = $2.39(\%CO + \%H_2) + 9.56 \times \%CH_4$

General equation for part excess air: $X = \dfrac{\dfrac{\%CO + \%CO_2 + \%CH_4}{\text{Part } CO_2 \text{ in flue gas}} - (100 + 1.89\%CO + .89\%H_2 + 7.55\%CH_4)}{2.39(\%CO + \%H_2) + 9.56\%CH_4}$

A, B and C determined separately. $X = \dfrac{A-B}{C}$

O_2 and heavy hydrocarbons neglected

Example: Assume gas analysis of CO = 23%, CO_2 = 5%, H_2 = 10%, CH_4 = 2%, and CO_2 in flue gas = 13.5%.

$X = \dfrac{A-B}{C} = \dfrac{222-168}{98} = \dfrac{64}{98} = .55 = 55\%$

Cu. ft air required for 100 cu. ft. gas = C = 98

" " " used " " " " " = A-B+C = 162

Cu. ft. burned gases from 100 cu. ft. gas = A = 222

FIG. 1.—Producer gas chart for determination of air required and excess air, for any gas with any per cent CO_2 in flue gas. Also actual and theoretical volume of burned gases from combustion of 100 cu. ft. of gas.

Any producer gas can be considered as a mixture of CO_2, O_2, CO, H_2, CH_4, N_2, and some miscellaneous hydrocarbons of complex form which exist in the form of tar vapors. These latter are a small proportion of the total combustible and are of such variety as to be almost impossible to analyze and base calculations upon. They are therefore neglected in the following discussion. As the per cent of O_2 is always very small being usually less than one-half of one per cent, its effect is also neglected. For practical consideration, therefore, the gas is treated as a mixture of the combustible gases CO, H_2, CH_4, and the inert gases, CO_2 and N_2.

For the combustion of any fuel there is a definite quantity of air theoretically required to complete the combustion. This quantity will hereafter be spoken of as C. If any air in addition to that required is permitted to enter the furnace chamber, this air will pass through the furnace as an inert gas taking no part in the chemical reaction and will appear in the products of combustion as nitrogen and oxygen. In discussing the amount of this extra air it is customary to express it as a proportion of the amount of air theoretically required. Writing this in the form of an equation, we have

$$\text{Part excess air in flue gas} = \frac{\text{Vol. of excess air}}{\text{Vol. of required air, or } C}$$

From this it is apparent that we must find a method of determining the volume of extra air in the waste gas and also the volume of air required for a given volume of the fuel to be burned. The volume of extra air will be the actual volume of waste gases minus the theoretical volume of waste gases which would have been obtained under perfect conditions without excess air, that is

Vol. of excess air = Actual vol. of waste gas minus Theoretical vol. of waste gases for perfect combustion

For simplicity this is expressed as: Vol. of ex. air $= A - B$.

$$\text{Therefore, per cent excess air} = 100 \times \frac{A-B}{C}.$$

It is evident that the part or fraction of CO_2 in the waste gases =

$$\frac{\text{Vol. of } CO_2 \text{ in waste gas}}{\text{Actual vol. of waste gas, or } A}$$

Transposing this equation we have a means for finding the actual volume of waste gases for

$$A = \frac{\text{Vol. } CO_2 \text{ in waste gas}}{\text{Part } CO_2 \text{ in waste gas}}$$

The theoretical volume of waste gas which would result from perfect combustion, or B, can be calculated from the chemical composition of the fuel as can also the theoretical amount of air required, or C.

The chemical formulae for the combustion of the gases involved are as follows:

$$2CO + O_2 = 2CO_2$$
$$2H_2 + O_2 = 2H_2O$$
$$CH_4 + 2O_2 = CO_2 + 2H_2O$$

Expressing these equations in terms of air required for the combustion of one cubic foot of each of the gases we have:

1 cubic foot of	+ cu. ft. air	Burns to cu. ft. CO_2	+ lbs. of H_2O	+ cu. ft. of N_2
CO	2.39	1	0	1.89
H_2	2.39	0	0.0501	1.89
CH_4	9.56	1	0.101	7.55

Adding these equations for the combustion of 100 cubic feet of any producer gas, keeping in mind the fact that the H_2O is lost by condensation in collecting sample we have the following:

Vol. air required for 100 cu. ft. producer gas $= C = 2.39(\%\,CO + \%\,H_2) + 9.56\%\,CH_4$

and

Vol. waste gases for perfect combustion $= B = 2.89\%\,CO + 1.89\%\,H_2 + 8.55\%\,CH_4$ plus non-combustible portion of gas

As the original gas is composed of the non-combustible portions plus per cent $CO + H_2 + CH_4$ and the volume of this gas under consideration is 100 cubic feet we can convert the above equation to the following form:

$$B = 100 + 1.89\%\,CO + 0.89\%\,H_2 + 7.55\%\,CH_4$$

The volume of CO_2 in the products of combustion from 100 cubic feet of gas will be the CO_2 originally in the gas plus that formed by combustion, that is:

Vol. CO_2 in waste gases from 100 cu. ft. of gas $= \%\,CO_2 + \%\,CO + \%\,CH_4$

Substituting this in our former equation for A which is the total actual volume of waste gases, we get:

$$A = \frac{\%\,CO + \%\,CO_2 + \%\,CH_4}{\text{part } CO_2 \text{ in waste gases}}$$

We now have each of the three quantities expressed in terms of the per cent of the various combustibles in the fuel and the fraction of CO_2 in the products of combustion. Substituting these values in the equation for excess air given above, that is, per cent of excess air $= 100 \times \frac{A-B}{C}$

we have the following general equation for excess air in the combustion of any producer gas with any fraction of CO_2 in the waste gases:

$$\% \text{ of excess air} = 100 \times \frac{\dfrac{(\% \, CO + \% \, CO_2 + \% \, CH_4)}{\text{part } CO_2 \text{ in flue gas}} - (100 + 1.89\% \, CO + .89\% \, H_2 + 7.55\% \, CH_4}{2.39 \, (\% \, CO + \% \, H_2) + 9.56 \, \% \, CH_4}$$

As will be noted, when mathematically expressed, the formula is by no means a simple one and so the chart was made to simplify its solution. The chart is divided into three major portions, each of which furnishes the value for one of the quantities, *A*, *B* and *C* considered above.

To find the value for *A* begin in the lower left hand corner with the proper percentage of CO, project vertically to the diagonal line representing the percentage of CO_2 in the producer gas and from here project horizontally to the diagonal line in the opposite direction representing the percentage of CH_4 in the gas. From this point project vertically to the series of radial lines in the upper left hand portion of the chart to the line representing the percentage of CO_2 in the flue gases. From this point project to the right and read the value of *A*, which is the actual volume of waste gases resulting from the combustion of 100 cubic feet of producer gas.

To find *B* start with the proper percentage of CO in the upper right hand portion of the chart, project to the line representing the percentage of H_2 and then down to the line representing percentage of CH_4. From here project horizontally and read the value of *B*, which is the theoretical volume of waste gases for perfect combustion. The difference between *A* and *B* is the actual volume of excess air used.

To find *C* start with the proper percentage of CO in the lower right hand portion of the chart, project upward to the proper H_2 line, then horizontally to the proper CH_4 line and from there vertically to read *C*, which is the volume of air required to burn 100 cubic feet of the gas in question.

With a little study of the system used in the chart and a little practice, it will be found that satisfactory results can be obtained in a very few minutes and with very little difficulty. If care is used, the results obtained from the chart will be as accurate as the gas analysis is likely to be, which is sufficient for all practical purposes.

Discussion

MR. CARTER: May I call attention to the fact that if any dependence is placed upon the amount of carbon dioxide in the escaping gases it will be necessary to consider that if sodium carbonate is used in the melt, the carbon dioxide carried by that sodium carbonate is likely to appear in the escaping gases, and the amount of it from that source will depend entirely upon the vigor of the reaction which is taking place at that time, so that the mere presence of a given percentage of carbon dioxide in escaping gases will be an erroneous foundation on which to build a very elaborate calculation in regard to excess air.

Mr. Smith: The amount of carbon dioxide appearing in the flue gases that comes from the chemical reaction of the batch is so small for practical purposes that it cannot be detected.

Mr. Carter: It very largely depends on the nature of the batch and the way it is put in. In the furnace with which I am familiar we have a periodic arrangement, that is, the batch is charged, the reaction proceeds for a certain length of time and then the melted material is moved. Under those conditions the amount of carbon dioxide appearing in the flue gases at certain stages of the reaction is a very considerable proportion of the total. Cases have been known in which carbon dioxide from the sodium carbonate of the batch has caused the analysis of outgoing gases to show 10% more CO_2 than it would have done if none had been derived from that source.

Chairman: I can see that if the reaction is taking place almost at one time and then it is melted down, quite a bit may be given off at once, whereas if the fills are made at regular intervals and the samples taken all along the port side of the tank and an average taken, it might be very, very small.

G. M. Peltz:[1] The point brought up by Mr. Carter is of interest and importance, not so much because of the magnitude of carbon dioxide which will be produced in most glass tanks, but because it brings up the importance of taking into account the practical conditions met with in a specific application of any general theory or calculation, such as that presented in my paper.

It should be noted that the purpose of my paper is to present only a simplified method of performing a mathematical calculation and I have not gone into the practical questions of obtaining the necessary gas samples and analyses. The chart, which was presented, applies to the general combustion of producer gases and was not intended exclusively for the glass business or any other business. It will, therefore, be necessary in considering its use under specific conditions to carefully consider what effect these conditions will have upon the results.

Replying specifically to the point raised by Mr. Carter I have made a rough calculation to determine approximately the magnitude of the carbon dioxide given off by a soft lime glass batch. Assuming a batch containing 22% sodium carbonate about 10% of the weight of this batch will be given off as carbon dioxide which, of course, mingles with the flue gases. Assuming a batch to cullet ratio of 1 to 1 it is apparent that the weight of CO_2 will be only 5% of the weight of the fill. Expressing this

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[1] Rec'd March 31, 1924.

in volumes we find that each pound of fill will produce 0.4 cu. ft. of CO_2. If 1 lb. of coal in the form of producer gas is required to every pound of fill, this will represent approximately 70 cu. ft. of producer gas which will require at least an additional 70 cu. ft. of air and will burn to at least 120 cu. ft. of non-condensible waste gases. About 17 cu. ft. of this total will be CO_2. It is apparent, therefore, that the CO_2 given off by the batch is not likely to be more than one-half of 1% of the total volume of waste gases nor more than $2^1/_2$% of the total volume of carbon dioxide. There may be special cases, such as mentioned by Mr. Carter, which might depart considerably from the above rough calculations, but such cases would be rather exceptional and would have to be treated as such.

As mentioned above it has not been my intention in this paper to go at length into the questions of obtaining representative gas samples and analyses for this question has been covered in many other books and articles. It is obvious, of course, that the results obtained from my chart cannot be more accurate than the analyses. It has been my experience that great care must be used in taking proper samples and that the errors due to such causes as non-representative samples, leakage, absorption of CO_2 by water, incomplete absorption in the Orsat apparatus, etc., are likely to result in greater errors than will be produced by gases given off from the batch.

In regard to the question of obtaining proper samples each specific case must be considered separately, but I have found it desirable to observe the following general rules in taking samples from glass tanks:

(1) The sample should be taken from a part of the furnace which is under positive pressure so as to avoid all possible leakage.

(2) Sample must not be drawn through an iron pipe which is permitted to get hot for this will change the gases coming through it. A water-cooled iron pipe or a porcelain tube is preferable if the sample is taken from a hot portion of the furnace.

(3) The sample should be drawn from a portion of the furnace where the gases are passing at a considerable velocity and where there is the greatest possible agitation which will produce thorough mixing. A good point for this is in the down-take between the port and the top of the checkers.

(4) Samples should never be allowed to remain for any length of time in a container which contains water for this results in a surprising amount of CO_2 being absorbed by the water.

(5) In general, samples should be analyzed as soon as possible after taking and reagents used in the Orsat apparatus should be renewed frequently.

CORNING GLASS WORKS
CORNING, N. Y.

THE DETERMINATION OF POROSITY OF CHINA BY THE WATER SOAKING METHOD[1]

By Edward Schramm

ABSTRACT

Comparative tests show that prolonged soaking is more effective than boiling in attaining saturation of nearly vitrified ware, and a period of 4 days' immersion in cold water is recommended.

The subject of determining porosity has been exhaustively treated by Washburn and his co-workers,[2] who developed standard methods using liquids and gases as the pore-filling medium. Many of these methods require special apparatus and technique. Our problem was to make porosity determinations on vitrified china as a means of plant control and to make the method available to untrained men. For this purpose we carried out a brief study of the water soaking method on glazed and unglazed samples of vitrified and nearly vitrified ware. The samples were broken from plates having a thickness of approximately 0.2 inch. The ware used had a specific gravity of 2.36 to 2.40. The aim of the work was threefold: (1) To determine a suitable size of test-piece; (2) To compare the results by boiling and by cold soaking; (3) To ascertain whether the test could be applied to a glazed piece without grinding off the glaze.

For the purpose of the test we selected three pieces of properly fired ware, three of decidedly underfired, and three of very badly underfired. These are designated A, B, C, respectively. The biscuit plates were broken in two and half of each plate glazed and fired in the glost kiln, a procedure which, it was assumed, would not alter the porosity. Pieces were broken from the center of the plates in such manner that all of the edges were fractured. The results on different periods of exposure, etc., represent separate runs on identical test-pieces which were dried and reweighed between determinations. All weighings were made on a chemical balance; for the wet weighing the piece was quickly dried with a damp towel and introduced into a weighing bottle, thus avoiding loss during the weighing. The results are given in Tables I and II.

The general conclusions drawn from the above data are: (1) Prolonged soaking is essential and boiling does not hasten the penetration sufficiently to permit dispensing with the soaking period. This result is directly contrary to that reported by Foster[3] working on porous clay tile. The necessity for the soaking period is pointed out by Washburn and Footitt.[4] (2) No higher results are obtained by a combination of boiling and long soaking than by soaking alone. The boiling may therefore be omitted, thus simplifying the test and avoiding the dangers of loss by solution and gain by rehydration as found by Washburn.[1] (3) While no attempt has

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[1] Presented at the Atlantic City Meeting, Feb., 1924 (Whitewares Division).

[2] *Jour. Amer. Ceram. Soc.*, **4** [11], 916; [12], 961; *Ibid.*, **5** [1], 48; [2], 112; [8], 527.

[3] *Ibid.*, **5** [11], 788.

[4] *Ibid.*, **4** [12], 979.

TABLE I

PER CENT ABSORPTION LARGER TEST-PIECES

BISCUIT

No.	Weight of piece, grams	Boil 2 hrs. Cool quickly	Boil 4 hrs. Cool quickly	Boil 6 hrs. Soak 16 hrs.	Soak cold 96 hrs.
A-1	12.1100	0.05	0.05	0.10	0.07
A-2	23.4897	0.01	0.04	0.03	0.01
A-3	12.0270	0.07	0.11	0.15	0.00
B-1	18.1686	0.94	1.43	1.85	1.95
B-2	24.5646	0.84	1.01	1.71	1.91
B-3	16.8330	0.95	1.20	1.85	2.02
C-1	14.1830	2.03	2.34	2.43	2.64
C-2	16.2885	1.70	2.10	2.61	2.64
C-3	15.8239	1.91	1.94	2.28	2.51

GLAZED

No.	Grams	Boil 2 hrs. Cool quickly	Boil 4 hrs. Cool quickly	Boil 6 hrs. Soak 16 hr.	Soak cold 96 hrs.
A-1	26.0286	0.005	0.006	0.008	0.011
A-2	19.0122	−0.011	−0.005	0.0	0.0
A-3	11.6485	0.0	0.0	0.0	0.0
B-1	17.5543	0.40	0.57	1.30	1.65
B-2	25.6868	0.67	0.59	1.42	1.67
B-3	20.0985	0.41	0.44	1.11	1.57
C-1	17.1429	1.06	1.00	1.92	2.13
C-2	11.1353	1.29	1.30	1.97	2.20
C-3	20.3000	0.88	0.95	1.80	2.00

TABLE II

PER CENT ABSORPTION SMALLER PIECES

BISCUIT

No.	Weight of piece, grams	Boil 6 hrs. Cool quickly	Boil 6 hrs. Soak 70 hrs.	Soak cold 98 hrs.
A-1	8.8360	0.10	0.10	0.08
A-2	5.9220	....	0.08	....
A-3	6.6760	....	0.10	....
B-1	8.7100	1.49	2.16	2.04
B-2	8.2800	1.33	1.86	1.87
B-3	6.4750	1.47	1.90	1.92
C-1	6.4250	2.34	2.73	2.73
C-2	9.3940	2.14	2.57	2.55
C-3	7.5880	2.20	2.61	2.50

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[1] *Jour. Amer. Ceram. Soc.*, **4** [12], 971.

TABLE II (*continued*)

PER CENT ABSORPTION SMALLER PIECES

GLAZED

No.	Weight of piece, grams	Boil 6 hrs. Cool quickly	Boil 6 hrs. Soak 70 hrs.	Soak cold 98 hrs.
B-1	9.6330	0.70	1.61	1.58
B-2	8.6400	1.04	1.69	1.69
B-3	8.9870	0.65	1.54	1.56
C-1	10.4745	1.39	2.06	2.10
C-2	8.7090	1.63	2.31	2.15
C-3	8.8940	1.64	1.94	1.96

been made to determine true porosity by a standard method, the fact that similar values were obtained with test-pieces of different sizes indicates that saturation must have been practically complete. (4) The saturation of the glazed pieces was 80% that of the unglazed so that it is possible to estimate the porosity of a small glazed piece with fair accuracy provided fresh fractures are exposed on the edges.

The recommended procedure for determining porosity of china by water absorption is to break out a test piece of such shape that no part shall be distant more than $^3/_8$ inch from a fractured edge; weigh this piece accurately on a chemical balance, soak in cold water for four days, dry quickly with a damp towel and weigh in a stoppered weighing bottle. In this manner the simple water-soaking method may be made to give consistent results and we have been able with its aid to follow out vitrification range curves passing from underfire to overfire, the results checking the more accurate determination of bulk specific gravity.

ONONDAGA POTTERY CO.
SYRACUSE, N. Y.

COMPARATIVE TESTS OF POROSITY AND SPECIFIC GRAVITY ON DIFFERENT TYPES OF REFRACTORY BRICK[1]

By E. E. Pressler[2]

ABSTRACT

Comparative data of porosity and specific gravity on several types of refractory brick are presented. Apparent porosity is obtained directly by the water absorption and air expansion methods. Total porosity is calculated from the true specific gravity and apparent specific gravity is calculated from the observed porosity values.

The results indicate (1) a more accurate measurement of open pore space in bricks by means of the air expansion method than by water absorption, and (2) the absence of sealed pores in some types of refractory brick.

Purpose of the Investigation

In order to study the relative value of porosity and specific gravity data obtained by different means, comparative tests were made upon several types of refractory brick.

Procedure

Porosity was determined directly by the water absorption method and by means of an air expansion porosimeter.[3] True specific gravity was determined by the pycnometer method upon the ground brick material. Apparent specific gravity was calculated from the observed porosity values, and total porosity was calculated from the true specific gravity. All calculations were based on the same weight and volume data, and uniform methods of testing were followed throughout, in order to render the results comparable.

Method of Testing Porosity by water absorption was determined by partially immersing the bricks in water and boiling for 1 hour, and then immersing completely and boiling for 5 hours. A soaking period of 24 hours was allowed.

Porosimeter tests were made upon the bricks dried at 110°C and cooled under a bell jar containing calcium chloride. The air in the auxiliary air container was artificially dried.

The true specific gravity determinations were made upon material passed through a 100-mesh sieve and dried at 110°C to constant weight. Tests were made upon samples of from 5 to 8 grams, and toluene was used as the reference liquid.[4] Weighings were made at constant temperature, and the specific gravity of toluene was determined directly for the temperature of weighing. Entrapped air was removed by means of a vacuum pump.

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[1] Published by permission of the Director, U. S. Bureau of Mines.

[2] Ceramic Assistant, Ceramic Experiment Station, Bureau of Mines, Columbus, Ohio.

[3] The apparatus is described under the title "A Simple Brick Porosimeter," *Jour. Amer. Ceram. Soc.*, **7** [3], 154(1924).

[4] Toluene is preferred to water because it is relatively less active with the brick material. It has the disadvantages, however, of a higher vapor pressure and coefficient of expansion than water at room temperatures.

Results

The results obtained for series of different types of bricks are given in the tables.

TABLE I

COMPARATIVE RESULTS OF POROSITY AND SPECIFIC GRAVITY

SERIES A—SILICA BRICK

Brick No.	Per cent absorption	Porosity		Per cent sealed pores	
		Porosimeter	Total calcd. from sp. gr.	Absorption	Porosimeter
1	27.12	28.31	28.34	1.22	0.03
2	27.60	27.98	28.04	0.44	0.06
3	27.55	28.22	28.07	0.52	−0.15
4	26.78	28.76	28.64	1.86	−0.12
5	27.06	27.61	27.79	0.73	0.18
6	26.79	27.19	27.10	0.31	−0.09

Brick No.	Specific gravity calcd. from porosity		
	Absorption	Porosimeter	True
1	2.293	2.332	2.333
2	2.309	2.321	2.323
3	2.312	2.334	2.329
4	2.300	2.327	2.322
5	2.306	2.324	2.330
6	2.306	2.310	2.307

TABLE II

COMPARATIVE RESULTS OF POROSITY AND SPECIFIC GRAVITY

SERIES B—MAGNESITE BRICK

Kiln level	Per cent absorption	Porosity	
		Porosimeter	Total calcd. from sp. gr.
Top	24.91	25.69	25.69
Top	29.35	30.56	30.56
Middle	26.81	27.71	27.85
Middle	24.65	25.43	25.61
Bottom	25.66	25.96	25.96
Bottom	28.43	29.53	29.53

Kiln level	Per cent sealed pores[1]	
	Absorption[2]	Porosimeter[3]
Top	0.78	0.00
Top	1.21	0.00
Middle	1.04	0.34
Middle	0.96	0.18
Bottom	0.30	0.00
Bottom	1.10	0.00

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[1] Possibility of calculating the sealed pores from the true and apparent specific gravities was first developed by Ross C. Purdy, *Trans. Amer. Ceram. Soc.*, **10,** 367 (1908); *ibid.*, **11,** 69(1909).

[2] Calculated from data obtained in porosity by absorption method.

[3] Calculated from data obtained by porosimeter method.

Kiln level	Specific gravity calcd. from porosity		
	Absorption	Porosimeter	True
Top	3.497	3.552	3.552
Top	3.485	3.556	3.555
Middle	3.500	3.550	3.564
Middle	3.510	3.552	3.561
Bottom	3.529	3.558	3.556
Bottom	2.496	3.544	3.544

TABLE III

COMPARATIVE RESULTS OF POROSITY AND SPECIFIC GRAVITY
SERIES C—FLINT FIRECLAY BRICK

Cone of firing	Per cent absorption	Porosity	
		Porosimeter	Calcd. from true sp. gr.
4	23.98	26.28	27.74
5	23.54	26.58	29.41
6	23.74	26.65	29.44
9	23.16	25.94	29.68
11	22.65	25.40	31.48
12	22.34	25.63	32.57

Cone of firing	Per cent sealed pores	
	Absorption	Porosimeter
4	3.76	1.46
5	5.87	2.83
6	5.70	2.79
9	6.52	3.74
11	8.83	6.08
12	10.23	6.94

Cone of firing	Specific gravity calcd. from porosity		
	Absorption	Porosimeter	True
4	2.537	2.616	2.668
5	2.511	2.615	2.721
6	2.468	2.565	2.667
9	2.476	2.571	2.706
11	2.379	2.467	2.686
12	2.357	2.462	2.715

TABLE IV

COMPARATIVE RESULTS OF POROSITY AND SPECIFIC GRAVITY
SERIES D—PLASTIC FIRECLAY BRICK

Heat treatment	Absorption	Porosimeter	Calcd. from true sp. gr.
Soft Burned	21.91	22.84	22.84
Soft Burned	21.93	22.73	22.56
Medium Burned	20.50	21.19	21.44
Medium Burned	20.79	21.27	21.59
Hard Burned	12.61	15.68	16.00
Hard Burned	12.02	15.69	15.93

TABLE IV (*continued*)

COMPARATIVE RESULTS OF POROSITY AND SPECIFIC GRAVITY

SERIES D—PLASTIC FIRECLAY BRICK

Heat treatment	Per cent sealed pores		Specific gravity calcd. from porosity		
	Absorption	Porosimeter	Absorption	Porosimeter	True
Soft Burned	0.93	0.00	2.667	2.694	2.694
Soft Burned	0.63	−0.17	2.665	2.668	2.682
Medium Burned	0.94	0.25	2.635	2.653	2.661
Medium Burned	0.80	0.32	2.643	2.659	2.670
Hard Burned	3.39	0.32	2.564	2.651	2.661
Hard Burned	3.91	0.24	2.546	2.649	2.657

Discussion of Results

Series A. Silica Brick

This series consists of silica brick taken from different locations in a commercial kiln. The heat treatment ranged from cones 17 to 19.

Porosity by water absorption is seen to be lower than the corresponding porosimeter values. The porosimeter values compared with calculated total porosity, show the absence of sealed pores. These relations indicate that these bricks have no pores sealed to the air expansion effect, but that a certain percentage of pore volume remains "sealed" to water penetration effects.

Specific gravity values are more generally compared in silica brick than porosity values, since they indicate the effect of heat treatment more directly.[1] The apparent specific gravity, calculated from water absorption data, is found to be lower than the determined true specific gravity.[2]

Since the apparent specific gravity, calculated from porosimeter data of porosity, agrees within experimental limits with the determined true specific gravity, the porosimeter method may be used for obtaining approximately true values of specific gravity. This method has advantages over direct specific gravity determination, inasmuch as the testing procedure is more rapid and less exacting and requires no mutilation of the test specimen. It is particularly well adapted for use in kiln firing control.

Series B. Magnesite Brick

The magnesite brick were also taken from different locations in a commercial kiln. The heat treatment ranged from cones 16 to 18.

The magnesite brick show the same general behavior as the silica brick and the same observations apply. A correspondence between specific gravity and important physical properties of magnesite brick is pointed out by McDowell and Howe.[3]

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[1] The porosity of dry pressed brick depends primarily upon the pressure applied in forming, while specific gravity depends only upon the density of the material.

[2] A similar discrepancy between apparent and true specific gravity of silica brick is found by Office, *Jour. Amer. Ceram. Soc.*, **2** [10], 832–35(1919); Harvey and McGee, *ibid.*, **5** [4], 219 (1922).

[3] *Ibid.*, **3** [3], 184(1920).

Series C. Flint Fire Clay Brick This series of bricks was taken from different locations in a rectangular down-draft kiln showing an usually wide range of heat treatment. These bricks are flint fire clay grog bonded with plastic fire clay. They were machine molded from soft mud.

The observed porosity values show a greater disagreement than for silica or magnesite brick. Both the absorption and the porosimeter data, compared with calculated total porosity, indicate a certain percentage of sealed pores.

With progressive heat treatment, a decrease of open pore volume takes place concurrently with an increase of sealed pore volume. It is apparent, therefore, that neither open pore nor total porosity, considered alone, gives a positive indication of the state of the ware. Specific gravity values show no regular relation to degree of heat treatment. For these brick, it appears that exact indication of heat effect requires both porosity and specific gravity determinations, the latter values being used to calculate total porosity.

Series D. Plastic Fire Clay Brick This series consists of bricks taken from regular stock and classified as soft, medium, and hard burned. The composition is straight plastic fire clay. They were made by the stiff mud repress process.

The observed porosity values show a greater disagreement in densely burned than in softer burned bricks. The porosimeter values, compared with calculated total porosity, indicate a very slight development of sealed pores.

Specific gravity values appear less indicative of heat treatment than porosity values. For these brick, porosimeter values of porosity may be considered as representing total porosity, without significant error.

Conclusions and Observations

The following points are brought out:

1. Porosity by water absorption is lower than true open pore values, particularly in the case of densely burned brick.
2. Porosity values of silica and magnesite brick are less indicative of heat treatment than are specific gravity values.
3. Different types of fire clay brick show a marked variation in the volume of sealed pore space developed.
4. Specific gravity values, as such, are not reliable indices of heat treatment of fire clay brick, but may be useful to calculate total porosity.
5. Porosimeter values of porosity approximate total porosity of fire clay brick in some cases, but not in others.
6. An important observation is that the silica and magnesite brick are found not to develop sealed pores in the process of firing.

CERAMIC EXPERIMENT STATION
BUREAU OF MINES, OHIO STATE UNIVERSITY
COLUMBUS, OHIO

NOTES ON A COMPARATIVE TEST OF QUICKLIMES FOR SILICA BRICK MANUFACTURE[1]

By L. J. Trostel

ABSTRACT

In attempting to evaluate lime for control purposes in the manufacture of silica brick, it was found that the most consistent results are obtained by using a figure based on the *total* calcium oxide as compared with the A.S.T.M. *available* calcium oxide content. In addition, the particular test used serves as a practical basis for the comparison of the numerous quicklimes offered the silica brick manufacturer by lime dealers.

For some time it had been the practice in one of the plants manufacturing silica refractories of the writer's company to attempt to carefully check the quality of lime entering all green mud charges. For this purpose, each car load of quicklime upon arrival was analyzed for its available, or water soluble CaO and then from this the quantity was figured which would be necessary to add to the green mud charge to produce the percentage of CaO desired.

Owing to the great number of dealers offering supposedly high quality chemical quicklime and their contending claims it was felt that some practical plant test should be devised which would be applicable to all limes offered and serve as a basis of comparison.

Method of Use In this plant, as in most plants manufacturing silica refractories, the lime before being added to the crushed ganister, is slaked in batches of from 27 to 32 pounds in sheet iron tubs with revolving paddle stirrers. After a 15 or 20 minute mixing period with hot water, the slaked "milk of lime" is run out of the tubs, through a screen with $^1/_4$-inch openings and then into the green mud charge in the wet pan.

The screen serves to catch the unburned and overburned pieces, clinkers and other foreign material which did not slake during the above period.

Lime for silica brick manufacture must be of as high CaO content as is possible and in addition slake rapidly enough that it will all be converted to "milk of lime" in the usual 15 to 20 minute period in the slaking tubs.

Test of the Lime The test consists of obtaining the total weight of quicklime used during a day's run in the plant and analyzing a portion for the *total* CaO, as well as the *available* CaO, using A.S.T.M. methods throughout. Then all the residue from the above weight of lime, consisting of clinkers and overburned and underburned pieces which did not slake and were caught on the screens and remained in the bottom of the slaking tubs in the lime room, was saved, air-dried, weighed and analyzed for its total CaO content.

The data from these tests are shown in Table I.

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[1] Recd. April 4, 1924.

TABLE I

TESTS ON QUALITY OF VARIOUS QUICKLIMES

a	*b*	*c*	*d*	*e*	*f*	*g*	*h*	*i*	*j*
Test	Lime used	Total calcium oxide	Available calcium oxide	Actual calcium oxide used $= b \times c$	Residue recovered	Total calcium oxide in residue	Actual calcium oxide in residue $= f \times g$	Loss lime expected $= c - d$	Loss lime actual $= \frac{h}{e} \times 100$
No.	Lbs.	%	%	Lbs.	Lbs.	%	Lbs.	%	%
1	4550	94.4	89.6	4295	62.5	54.7	34.2	4.8	0.8
2	5398	94.8	80.7	5117	31.0	57.6	17.9	13.3	0.4
3	5032	92.3	84.6	4643	27.0	48.3	13.0	7.8	0.3
4	4168	92.3	86.8	3847	35.0	56.2	19.7	5.5	0.5
5	5265	91.0	84.9	4791	31.0	43.7	13.5	6.1	0.3
6	3996	93.3	80.2	3728	20.25	55.1	11.2	13.1	0.3
Av.	4735	93.0	84.5	4404	34.5	52.6	18.3	8.4	0.4

The most striking thing shown by these data is first, the rather large differences in column "*i*" and "*j*" and second, the regularity of column "*j*" as compared with "*i*." This means that the A.S.T.M. method for determining available lime is not suitable as a basis for comparison of limes for this process and that the total lime is much better. This led to basing the weight of lime added to a charge of green mud on the *total* CaO content of the quicklime, instead of the A.S.T.M. *available* content which had heretofore been the practice. The results justified this change in practice.

Previously, muds would often analyze as much as 3% lime, compared with the 2.25% calculated. Now a variation of 0.2% either way from the 2.25 calculated is the maximum found when close attention is paid to the process. Anyone acquainted with the manufacture or use of silica brick will readily appreciate the value of being able to control the percentage of lime in the brick so that neither low lime with resulting poor bond and insufficient quartz inversion and expansion result, nor high lime with lowered fusion point and the long train of ills that accompany this condition.

The practice of calculating lime on the available basis probably had its origin in the apparent similarity of the A.S.T.M. test to the slaking operation in the plant, both water treatments, and therefore the assumption that only the available CaO was slaking up in the mixing tubs and got into the brick. The difference, of course, lies in the theoretical conception of the available lime as compared with what constitutes the available lime as found by experience in this particular process.

According to the National Lime Association, by the available lime is meant that portion of the total oxide content of the lime, either quicklime, or hydrated lime, calculated as CaO, which is easily soluble in water and is thus available as a source of hydroxyl ions. It is true that the oxide content of the lime may be more available for one process than for another, the difference depending on the conditions for the reacting mixtures, etc. To illustrate, it is possible that a greater or less percentage of the oxide of the lime might be available in a causticizing reaction than would be available, for example, in a water treatment. If this is true a different method for determining the so-called available lime would be necessary for each process.

Actually, the real available lime in quicklime in the manufacture of silica refractories in this plant is not exactly that defined by the National Lime Association and detected by the A.S.T.M. method but includes some of the materials which are considered unavailable lime. This is due to the fact that the screens under the slaking tubs are large enough to allow fair-sized particles of some overburned lime (calcium silicate) and underburned lime (calcium carbonate) to pass through, and in such a test as the one described, these materials would get into the green mud and for all practical purposes become available lime.

The test just described has proved valuable in detecting whether, or not, the percentage of underburned and overburned stone, or clinkers is high, for these would be noticeable in the residue on the screens and the bottom of the slaking tubs and make the "lime efficiency" low. The test thus serves as a valuable comparative test in choosing a dependable, high quality quicklime from the numerous products offered the manufacturers of refractories by lime dealers.

General Refractories Co. Laboratories
Joliet, Illinois

NOTE ON SECONDARY EXPANSION OF FLINT CLAY

By Fred A. Harvey

ABSTRACT

Certain flint fire clays show a secondary expansion, which may amount to several per cent, at a temperature much below that at which dangerous expansion begins. Some specifications discriminate unjustly against brick containing fire clays of this type.

The purpose of this brief note is to establish the fact that certain fire clays show an expansion at a temperature considerably below that at which they begin to "overfire."

There are a number of specifications for first quality fire-clay brick which recognize the fact that a clay brick which begins to overfire at a temperature of 1400°C is not suitable for use at high temperature. This fact is granted without argument. The specifications, however, do not admit that there may be expansion from any cause except overfiring. For example, the A.S.T.M. "Definition" for High Heat Duty Fire-Clay Brick No. C27-20, states that when the brick are heated for five hours at a temperature of 1400°C they shall not show a permanent expansion on cooling of more than 1%.

When the United States Refractories Corporation first undertook to make a brick to meet this specification it was found that most of the test brick expanded considerably more than 1%. All the clays used had a softening point of cone 32 to 34, including the bond clay. A chance remark by Mr. Young, Superintendent of the Barrett plant, formerly in charge of the Woodland plant, put us on the right track in our study of this failure to meet the A.S.T.M. definition.

Some 9-inch brick had come from the kiln which measured only $8^7/_8$ inches long. Mr. Young explained this by saying that the brick were too light-burned to be full length. It was his experience that it takes heavy firing to bring the brick up to full dimensions. This observation was speedily established as a fact.

We can say definitely that a light-burned brick which contains any considerable percentage of Morgan Run Hard Clay will be from $^1/_{16}$ inch to $^3/_{32}$ inch shorter than the same brick when hard burned.

Some brick made to accentuate this property, measured $13^1/_2$ inches after being burned to approximately 2200°F (1204°C), and full 14 inches after being burned in our silica kilns to a temperature of 2650°F (1454°C). Yet there is not the slightest evidence of overburning. There are no spots showing distortion, there is practically no trace of vitrification having started, as would be the case with overburning.

J. Spotts McDowell also has observed this expansion of clay brick between what is called a light burn and a hard burn.

After we had the facts before us it was not difficult to make a brick which would consistently pass a specification even more rigid than the A.S.T.M.

definition. Yet the fact remains that a high heat duty brick made to pass this specification would be entirely unsuitable for many uses.

Is it reasonable to say that a brick burned to 2200°F is not a high heat duty brick while the same brick burned to 2400°F becomes a high heat duty brick?

The practical experience cited above is nicely corroborated by some laboratory tests made for us at Mellon Institute. Figure 1, Curve I, shows a typical volume-temperature curve for fire clay, Curves II and IIa show heat volume curves for Morgan Run hard clays. It will be noted that there is a contraction up to a temperature of about 1200°C then an expansion up to 1350°C then contraction to the highest temperature which could be reached. It is evident that even at 1500°C the temperature of overfiring has not nearly been reached. The clays have a softening point of about cone 33–34 and approximately the following chemical analysis. (Burned clay.)

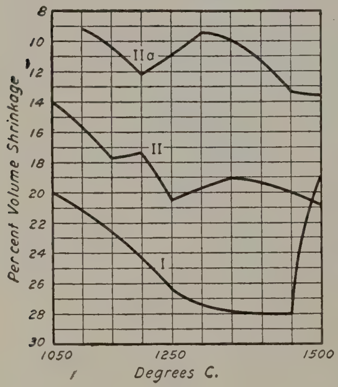

FIG. 1.

SiO_2, 49.5; Al_2O_3, 44.4; Fe_2O_3, 2.5; TiO_2, 2.1; CaO, 0.2; MgO, 0.1; Alkalies 1.2.

Figure 2, Curve I, made at a different testing laboratory exhibits the same characteristic. This chart was kindly loaned for the purpose of this note. It represents linear change during a load test. It will be noted that starting at 1250°F (677°C) even under a load of 25 lbs. per sq. in., the brick expands 1.2% until a temperature of 2236°F (1224°C) is reached when contraction again starts. There is then a period of constant length and final collapse at 2755°F (1513°C). It will be noted that the temperatures given are somewhat lower than those recorded at Mellon Institute.

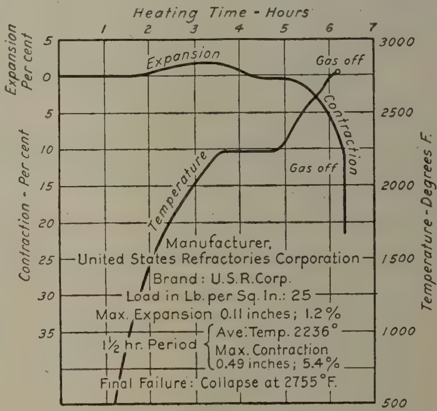

FIG. 2.

In some clays there is a secondary expansion, followed by contraction during heating, either in kilns or testing furnaces, which is entirely distinct from the expansion due to overburning. The expansion due to overburning indicates an inferior clay. This secondary expansion is an asset to the consumer in keeping walls and arches tight.

UNITED STATES REFRACTORIES CORPORATION
MOUNT UNION, PA.

INSULATION OF GLASS TANKS[1]

By W. K. Brownlee

The walls and bottom of a glass melting tank are insulated to give a longer life. The cause of rapid erosion must be determined before the remedy can be devised.

The tank blocks are more or less porous which gives opportunity for fluxing of the glass constituents with the clay of the tank blocks. The clay base undergoes alteration and is flushed away into solution exposing fresh surfaces to further reaction.

An outstanding feature of the effects of erosion, is the uneven vertical corrugations down the walls of the furnace and it was this that raised the question of insulation as a means of preventing or reducing to some extent the convection currents that are moving downward over the inner surface of the clay walls drawing down with them the most active fluxes from the hot surface. The walls of a pot suffer less from erosion than the walls of a tank, and it is possible that because the direction of the currents in a pot is directly opposite to what it is in a tank, that pot walls are not subjected to the hottest action of the fluxes. In the pot the convection currents are going up the walls from a cooler temperature zone and in the tank they are going down the walls from the highest temperature zone.

It is true that the colder the walls of a tank, the more the convection currents are accelerated. It is also probable that a wall of even thickness (no matter how thick) would not stop convection currents. So in the construction of this experimental tank we exposed six inches of the top row of the blocks to the atmosphere, and increased the thickness of a wall toward the bottom to compensate for downward heat losses.

The flux block lining of the tank was 8 inches thick in the wall, and the size of the tank was 4 feet wide, 6 feet long and 2 feet deep. The bottom was of 12-inch flux blocks, 12 x 18 x 24 inches. These were placed on solid masonry (fire brick), 24 inches thick under which was a course of Sil-O-Cel, $2^1/_2$ inches thick. The base was 13 inches larger than the space covered by the tank blocks. We then placed a 9-inch wall of good high grade fire brick laid tight and neat against the outside of the lining, 4 courses high. Then the thickness of this lining was reduced to 6 inches for two courses of brick in height, the finish was a row of brick $2^1/_2$ inches thick. Outside of all this was a facing of Sil-O-Cel ($2^1/_2$ inches thick) and steel bracing was outside of all masonry.

The tank was operated for 30 days at 2500° to 2600°F, melting from 1500 to 1600 pounds of raw batch without cullet, each 24 hours.

Fixed amounts of batch were introduced at regular intervals, in one end of the furnace, and the melted glass was ladled or gathered from the other

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[1] Presented at the Atlantic City Meeting, Feb., 1924 (Glass Division).

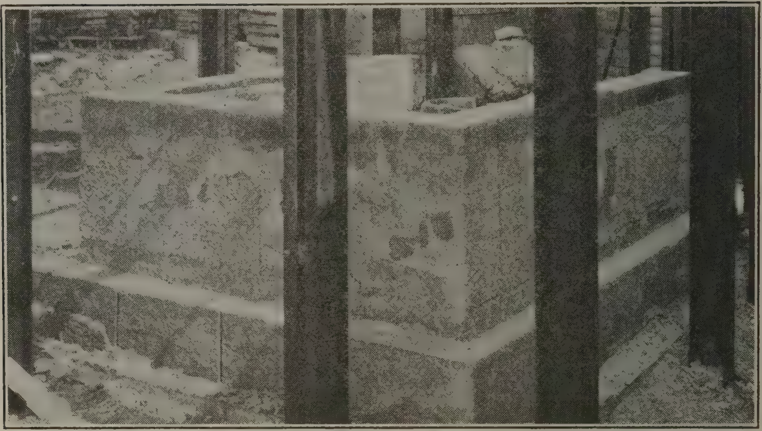

FIG. 1.

This photograph shows a glass melting tank four feet wide, six feet long and two feet deep.

The walls and bottom were insulated with fire brick next to the tank blocks and Sil-O-Cel outside of the fire-brick wall. The furnace operated at melting temperature for thirty days melting 1650 lbs. of bottle batch (no cullet used) each day. The new batch was filled on top at end which is removed, and ladled out of cylinder which was, when in position, near the end wall opposite from the wall removed. The wall linings were culled blocks and not specially burned, rather underburned, which was the main reason for calling them culls.

The purpose of the experiment was to determine if by insulation, increasing in thickness near the bottom, convection currents that evidently are responsible for vertical corrugated lines of corrosion could be retarded or eliminated. The appearance of the blocks clearly indicate that either convection or surface tension or both was eliminated greatly. The cracks in the end wall are probably due to shrinkage of the underburned clay. Glass at some joints did show through but progress was effectively interrupted by the fire-brick wall, as there was only a trace of metal outside of flux blocks.

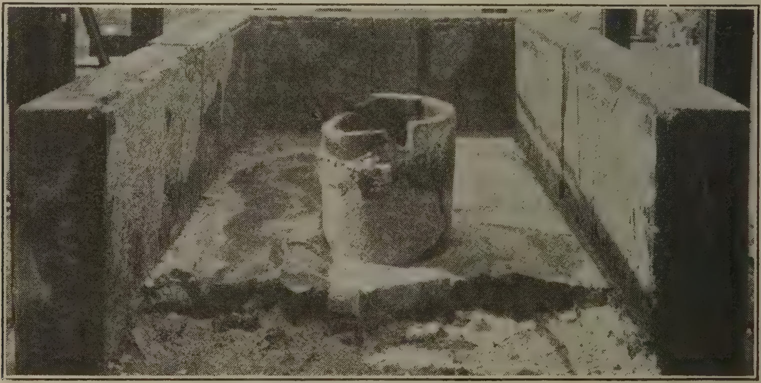

FIG. 2.

end from a cylindrical ring with holes in the bottom for passage of the glass to the ring. In other words the tank was operated as a continuous melting furnace for 30 days.

At the end of this period the fire was let out for observation of the action of the operation on the tank walls.

There was no evidence of vertical lines of erosion, or any loss of metal through joints or masonry.

In discussing this question with glass manufacturers, we find a number that see much merit in the idea. Some raise the question of leaks through the wall and the answer to this is, a high grade fire-brick wall of the right quality of clay will not wear out or leak glass through it, until it becomes exposed to the action of fluxes, and this will not occur until the furnace lining has been removed by erosion, and loss through erosion on the lining will be reduced correspondingly to the retarding of convection currents.

BUCKEYE CLAY POT CO.
TOLEDO, OHIO

Discussion

MR. CRAWFORD: How much corrosion was there in the block in that period?

MR. BROWNLEE: In the 30 days there was no noticeable corrosion at all.

MR. CASSELMAN: I do not comprehend your explanation for the absence of the channels in the block.

MR. PAYNE (Chairman): As I understand it, as the glass came in contact with the wall of the tank it was cooled. Thus the glass was more dense after it was cooled than the glass near the center of the tank or underneath it, hence it would sink. When the outside wall of the tank was insulated the edges were not cool and, therefore, there was none of this downward movement at the sides and upward in the center and across the top.

MR. REED: Where could information be obtained as to specific gravity of glass at various temperatures from 200° up?

DR. INSLEY: I believe the Geophysical Laboratory has done some work on the specific gravity of other materials at high temperatures and perhaps on some silicate glasses, but not commercial glasses.

MR. REED: Inasmuch as this entire discussion hinges on the vertical flow of glass, and on the specific gravity, some very definite information should be used to back up the theory and results claimed. There is absolutely no information which has come to light which gives the specific gravity of glass at anywhere near 2000°F.

The possibility of the results that have been pointed out by this experiment are large enough to warrant test work to be carried on to obtain the specific gravity of glass at this temperature. It would at least more definitely vindicate those who favor glass-tank installation.

Mr. Yung: I wonder if it is a question of specific gravity or whether it is a matter of viscosity. It always seemed so to me, but I have never had an opportunity of trying it out. A number of people have taken the measurements of the glass temperature on the surface of the tank and at the bottom and on 42″ depths it was found to differ by as much as 400°C. The most noticeable place of corrosion, according to my observation, is over the throat of the tank, the throat block of course getting the greatest amount of corrosion, but also the block immediately over that throat block corroded away before the side blocks of the tank, and I have often wondered if perhaps that did not mean that we were drawing a larger tonnage over that surface than we did over the lower parts of the tank. There is always the thought, of course, that the temperature increases corrosion, but I think there are other factors which should be considered. The lower part of the tank may be so cold that perhaps there is very little motion of the glass there, consequently very little corrosion, not much pulling away of small particles of clay block from the surface and exposing new surfaces, whereas on the surface of the glass you have less viscosity and consequently a greater flow exposing a new surface continually which might perhaps explain the greater amount of corrosion at the metal line. The matter of insulation might help overcome this feature by increasing the amount of insulation in proportion to the drop in temperature of the glass from the surface to the bottom giving a more uniform temperature condition throughout the depth of the glass which would tend to move a greater mass of glass in the tank than just the surface.

Mr. Dixon: In every instance known where insulation has been used on the tanks, we found that it decreased the life of the tank very materially, that the blocks disintegrated very much more rapidly, and experience in this always brings up many things that are really mysterious to those engaged in the business.

Mr. Yung's suggestion about the corrosion around the throat is one peculiar result that is known to everybody employing tanks of this kind, that is, the double compartment tank. One tank may have a production of 50 or 60 tons a day going through the throat. Another may have 15 or 20 tons production a day going through a throat the same size and the 60-ton tank will last just as long as the 15-ton tank. That seems to absolutely contradict the natural result that might be looked for, and yet, it happens.

To prolong the life of the tanks, everybody has tried just the opposite of insulation. They have air blown on the outside of the blocks to cool them or use water jackets in order to prolong their life. There is an experience I had some years ago. An accident happened to the furnace and it had to be put out about five weeks after it was started. It was a breaking bridge wall, and all of the glass ran into the basement. When the furnace was cooled we found the walls were so badly eaten away in that five weeks that it was most astounding. It was the first time I had ever seen a furnace let out in such a short time, and I could not advise the owners of the tank whether to leave the blocks in or to replace them. They replaced them. I have had that experience several times since and I have come to the conclusion that the inside portion of the block is eaten away in a very few weeks. The outside 4 or 5 inches will last indefinitely if kept cool, so that it is proven that the thicker the walls the more rapidly they disintegrate.

One of the first tank undertakings in this country was a most ridiculous proposition. The window glass tanks that were built at Jeanette in 1887-88 were built by people who had no engineering capacity or knowledge of the subject whatever, and I was one of them. They made the walls of those tanks 39 inches thick, and in a few weeks all the blocks had sloughed off and all that clay material had gone into the glass until the tank walls were about 10 or 12 inches in thickness, and then it remained for an indefinite time.

What was the use of 39 inches of wall in a furnace of that kind?

These things all tend to convince me that insulation of the tank block walls is working in the wrong direction. If the walls of much thinner blocks are kept cool, it has been frequently demonstrated they will at least last longer in the outside portion. I have never seen a tank that was insulated that has run any length of time.

A six weeks' or four or five weeks' test, such as has been described here is not a test of sufficient length of time to prove anything. It should be a test of a year to give data for any positive conclusions.

MR. AURIEN: From my experience I would concur with Mr. Dixon. I feel that the inside of the blocks could be expected to have some protection by your glass devitrifying, or in a sense, a dormant glazing. Now if you heat the outside of the blocks the tendency is to keep that much hotter and bring fresh metal in contact with the newer clay at the surfaces. I think what we want is cooling instead of heating up to prolong the life of the furnace.

MR. YUNG: Mr. Brownlee happened to have talked with me on this matter some time ago, so that I am familiar with his idea and theory and to open the discussion I was simply presenting his idea to straighten out the thought and start the discussion. It seems to me that there is so much that is unknown about the life of a tank, the causes for failures in the tank, that I think it well to study the subject from the various angles. For example, the matter of the short life of a 39-inch block in a tank, which Mr. Dixon speaks of, might not have been due to the increased amount of heat on the inside surface as much as it was to poor construction of the block. As any of the clay men here will probably admit, it is also a rather difficult proposition to properly burn a 39-inch block and get a homogeneous burning throughout, and if it is not burnt properly the interior of the block will be soft and is not going to last very long. I only mention this as a factor to introduce some discussion which may come up later from the causes for failures of tanks, which I think is well worth discussing.

MR. DIXON: The insulation of the refining compartment is old. We have been doing it for years, ever since we started to build these two-compartment tanks. The insulation consisted of a brick wall outside of the tank block wall on the refining compartment. That has become very dangerous now because the man who runs the furnace has to run the glass hotter. The machine production requires hotter glass, and we have had to take the insulation off of the working compartment.

MR. FLINT: I just tried to jot down a few things from memory that we took from some tanks; some of them are the averages of a few hundred. Approximately 5% or 6% of the heat, as I recall it as the average, is used up in melting and bringing the glass up to proper temperature, and about 5 or 6% is taken out by the hot glass as it leaves the tank, which is necessary because it has to be used hot on the machines. The stack carries a little under 20% of the heat. In other words, putting it in dollars for every dollar's worth of heat you are expending about 19 or 20 cents on the stack. That is not all loss, because $^3/_4$ or more of this is used in mechanically lifting the products of combustion out of the down-going checker chamber. The rest of it is due to radiation.

In our practice approximately $^1/_2$% to $3^1/_2$% of the heat value of the gas is lost in excess air. That gives approximately 28% to 30% of the heat that is put into the tank. The rest of it is lost by radiation. This heat was distributed about as follows: Regenerators and the flues took about 6%; the regenerators themselves probably lost about 3%. In other words, 97% of what went in went back into the tank. Some of that we could have corrected by insulation. The flues took out some; the crown, as we calculated it, took around 20% or a little under, the front half probably takes 8% or 9% and the back half 9% or 10%, because it gets more of the direct flame, and the off-takes took more—nearly 15%.

You cannot say, however, that that is true of all off-takes; ours might be a little more chopped up than the rest, although I do not believe so. The off-takes represent as much surface to the air as the crown will and in such a way, like a radiator, that they give off the heat. The side and the bridge together take about 20% or a little under, according to the glass, the heat, etc., and the bridge takes about 10%.

If you are going to economize on fuel you will find it is a big loss.

We figure that there are only two ways to correct this: Increase the amount of glass that goes through the tank so that that which is exposed to the heat can take it up and pass it on to the used article. If you raise the amount of heat that the glass gets and increase it 10% to 20%, you are getting it directly back in your own pocket, but you cannot do that generally.

The stack can be improved a great deal. Some stacks have rather thin walls, some of the steel stacks may have a small layer of brick, and they could be protected some. That only represents 5%. Most of that is necessary to the crown, etc., it is possible and it has been done. To insulate, we shall take the worst one, the off-takes—the fire is going right into the off-takes from the tank and has practically got the temperature of the flame. It is a high potential for heat loss and there is plenty of surface for radiation. Those have been insulated—they are beginning to do it with steel plants and are successfuly doing it. I believe with Mr. Dixon that it is perfectly all right to insulate the front end of the crown, and I even feel that we can do it now with our high temperature. When it comes to the side wall and the bridge, we are buying bigger blowers and putting more of them on there, because the tank boxes that used to last are not lasting now and we are trying to do our best to hold them. The measurements we have taken of the amount of wind delivered to tanks for side wall and bridge wall cooling have indicated somewhat in a rough manner, although it is hard to check, that the tanks with the least amount of wind are not doing quite so well. When we give them more wind we feel that we are getting better results out of them. If the flues, which are sometimes in damp ground, which is one of the nicest conductors of heat there is, could be insulated and water-proofed, it would help out. I find that the Illinois Pacific Glass Company, who are burning oil, have insulated a 12-inch crown with two layers of silica on top and insulated their off-take and they have done that for two fires at least. Well, if that's the case I do not see why—they insulated, by the way, the back end as well as the front end of the crown—I do not see why we could not go part way on that. I do not know that I would insulate the back end as it is such a proposition but I am just citing it as a fact. It has been done and has worked but I do not know anybody who has successfully insulated a flux block and kept the block there.

Mr. Brownlee: The discussion is mostly unfavorable to the idea proposed. I observe that the prevailing thought is that the insulation is sure to create a higher temperature in the blocks which will cause the clay to be more easily attacked as evidenced by the more rapid corrosion when excessive temperatures are used. As a matter of fact just the reverse of this is true.

Due to cold bottoms and side walls of glass tanks a rapid movement of the metal is set up over an area that represents about one-third of the total melting area. This of course reduces the time factor for melting, to one-third of what it would be, if the body of glass was all equal in temperature and viscosity, so under a slower and more uniform movement of the entire body of glass a *lower temperature* would, with the *increased time* allowed for the melting, be used.

This slower and more uniform movement of the entire body of glass cannot be obtained by cooling the walls and bottom. The cooling of the side walls does produce convection currents or rapid precipitation down the walls, also a surface tension of glass on clay, which probably removes the clay very rapidly while the wall is of full thickness. It may be that at this time, surface tension is all on clay and it may be that when the wall has worn to a thinness through which sufficient cooling can be transmitted, the surface tension is removed from the clay wall and the tension is then on the glass which is held congealed on the wall. If clay walls should not be kept at a high temperature, how was glass ever made in pots profitably? Pots do not suffer from corrosion as do tank walls, and yet all the temperature must be conducted through the walls, and if it were not for the shrinkage cracks that come on the inner face of pot walls, due to sudden cooling when batch is introduced, the pot walls would last as long or longer than tank walls.

This is due to proper heat conditioning of clay which is a natural sequence with pots and clay to withstand the action of glass should be burned to a temperature in excess of the temperatures to be used in melting glass. This will insure against physical change through shrinkage, and greatly decrease absorption of alkalies.

If we were to attempt to burn tank blocks to the degree of temperature required to condition them the best, we would first have to consider the practical dimensions of blocks that could successfully be burned to the right degree without excessive losses, and the difficulty of reheating when placed in the tank walls.

I am of the opinion that this can be done with blocks that do not weigh over 125 lbs., and suggest these blocks be not over 8 inches thick, 12 inches wide, and 18 inches long, or even less than this, say 8 x 8 x 12 inches. The number of joints is not as important as to get the general condition correct to make insulation do in the glass business, all that is possible for it to do in any other line. Insulation does not create temperatures that are disastrous to clay blocks. The temperature that does is created from another source which is desirable to reduce to the advantage of the clay blocks and conservation of fuel.

PREPARING AND SPRAYING A GLAZE SLIP WITH ESPECIAL REFERENCE TO THE CONTROL OF THE VARIOUS OPERATIONS[1]

By Robert Twells, Jr.

ABSTRACT

The article describes methods at the Champion Porcelain Company in glazing porcelain cores for spark plugs. One-day requirement of glaze slip is intimately mixed and ground in a pebble mill to pass 325 mesh, then stored separately and gently agitated for several days while firing, specific gravity and viscosity tests are being made. Careful records are kept regarding each batch. Some of the problems met in the preparing and spraying of the glaze slip are described.

Introduction

The application of a coating of slip to the surface of the ware is an important step in the manufacture of many ceramic products. At the Champion Porcelain Company considerable attention has been given to one phase of this subject: namely, the spraying of a thick coating of glaze slip on to a dry, unfired porcelain body. The ware in this case consists of spark-plug cores which present an unusually difficult spraying problem. The requirements are: (1) That the core be sprayed completely with the exception of the shoulder, the neck, the cap, and the bore (Fig. 1). The shoulder and cap must be kept free from glaze to prevent the cores from sticking to one another and to the sagger in firing; and, more important, the shoulder, cap, and neck must conform to standard dimensions within a limit of tolerance of 0.008 of an inch. Obviously such close limits could hardly be maintained with glazed surfaces especially if the spraying were uneven. (2) Between the glazed and unglazed surfaces the dividing lines must be straight, distinct and at the same place on every core; and (3) a spark-plug porcelain requires an abnormally heavy coating of glaze slip owing to the nature of the body and its high maturing temperature. The glaze itself melts about cone 11 down; the body does not vitrify until about cone 17. Between these temperatures the body readily absorbs a considerable

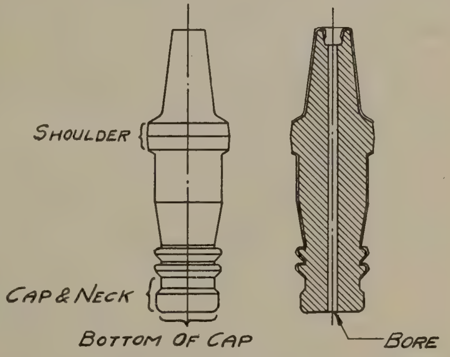

Fig. 1.—Sketch showing the parts of the spark-plug, porcelain core which are required to be glazed. This is indicated by the double outline of the cross-section.

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[1] A contribution from the Research Division of the Champion Porcelain Company and the Jeffery-Dewitt Insulator Company. Presented at the Atlantic City Meeting, Feb., 1924 (Whitewares Division).

portion of glaze, and would suck bare any spots too thinly sprayed. On the other hand the slip cannot be applied too heavily or the glaze would flow in firing and collect on the lower portions of the core.

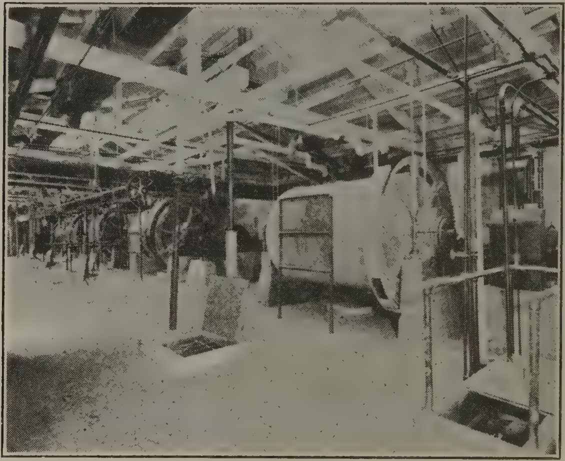

FIG. 2.—View of one section of the mill room.

Glaze Slip Preparation

Intimate mixing and thorough grinding are accomplished in a pebble mill 6 x 8 feet revolving at 15 r.p.m. (Fig. 2). The mill is lined with sillimanite porcelain bricks and carries five tons of balls made of the same body. The balls are kept within certain size limits and the same amount of materials and of water used. This gives a finished slip of a definite specific gravity and ground to pass through a 325-mesh lawn.

The mill is discharged into a blunger 9 x 9 feet situated in the floor below the mill. The mill is thoroughly washed with a measured quantity of water and the washings added to the slip in the blunger.

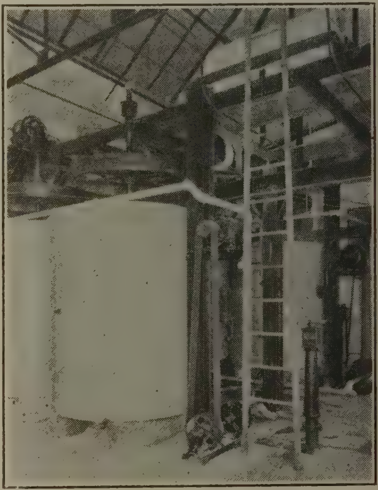

FIG. 3.—View of a section of the glaze slip storage room, showing the overhead location of the lawn, the storage tanks, the method of agitation of the slip, and the two centrifugal pumps for forcing the slip through the supply line.

Glaze Slip Storage Room and Circulation System

From the blunger the slip is passed through a hexagonal revolving lawn for removal of foreign particles coarser than 120-mesh and then into one of four storage tanks (Figs. 3 and 4). These are wooden tanks each 6 feet 4 inches by 5 feet holding one mill charge. Four semicircular blades rotating at 30 r.p.m. near the bottom of the tanks cause a current in the slip to rise at the tank's outer edge and fall at the center. The slip is thus allowed to age until required for use and meanwhile corrected for specific gravity and viscosity.

The slip is withdrawn by means of a centrifugal pump from the bottom of a tank, forced through a two-inch supply pipe extending over each spraying machine and returned to the same storage tank through a pipe extending down to within eighteen inches of the tank bottom. The slip thus circulates over the hopper of each spraying machine, and can be drawn into the hopper as required for use.

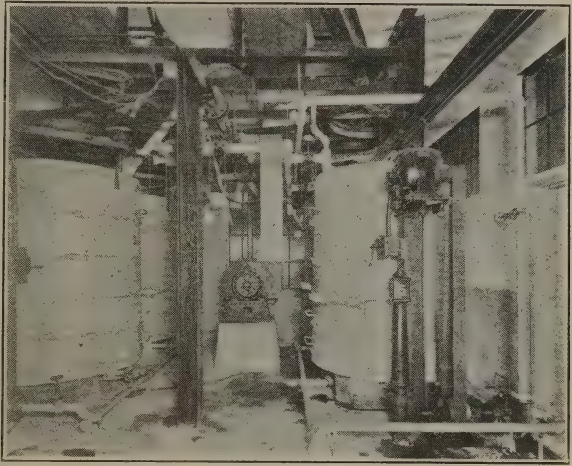

Fig. 4.—Another view of the glaze slip storage tanks. Note especially the pipes through which the slip is circulated to the spraying machines.

Spraying Equipment (Figure 5)

There are 10 spraying machines each with 20 spindles set vertically on a 11 $^5/_8$-inch circular revolving table. Inside of the glaze hopper is a smaller revolving hopper which serves the double purpose of lawning and agitating the slip. Each of the vertical spindles rotates on its axis as the table revolves, thus exposing the complete circumference of the core as it passes the spraying nozzles. There are two nozzles to a machine, one set to spray the upper and one the lower parts of the core. The slip is atomized by compressed air at a definite uniform pressure. Galvanized iron guards hinged at one end for easy adjustment protect the portions of the core which are to be left unglazed. The cores are packed directly from the spindles into carborundum saggers (Fig. 6), the bottoms of which have been

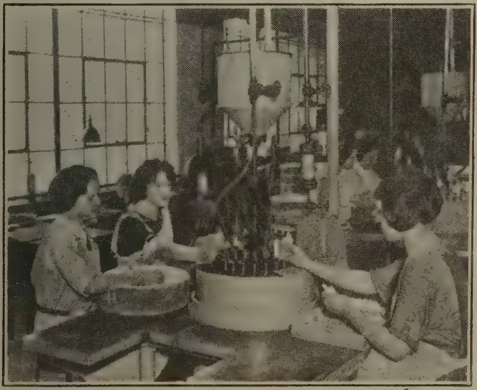

Fig. 5.—One of the spraying machines.

freshly painted on with an organic paste. This paste dries and holds the cores firmly upright while the sagger is being trucked about and being loaded on the kiln cars.

Figure 7 shows the method employed for glazing the cores before the present spraying system was installed. The core was held, while being dipped, by means of air pressure applied against the inside of the bore.

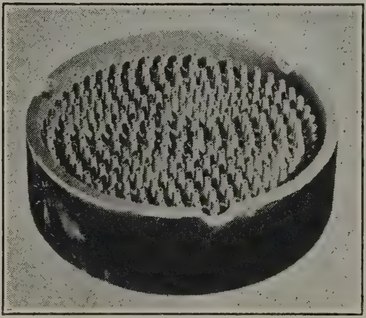

FIG. 6.—A sagger filled with sprayed cores ready for the kiln.

Methods of Control

(1) The first control test consists of careful chemical and physical tests of all glaze materials before being released for use.

(2) The next step is determination of the water content of each material allowance made for moisture.

(3) For each mill of glaze slip, a card is filled out giving the glaze number, the amount of each ingredient, the bin from which each is to be taken, the length of time of grind, and the amount of water to be added in grinding and washing. This card is given to the foreman in charge who checks each item as it is weighed. He fills in the mill number, the date, and the time of starting and stopping the grind. The card is then returned, checked, and filed.

(4) At the finish of the grind, a sample of the slip is sent to the Process Laboratory for a fineness test through a 325-mesh lawn; the amount failing to pass is noted.[1]

(5) Another sample is taken after the slip is in the storage tank. This is divided into two parts.

(*a*) One part is sent to the Process Laboratory where 25 regular cores are dipped in it. These are hurried into a kiln and are out, ready for examination, before the glaze mix itself is needed for production. These fired-porcelain cores are tested for impact strength and for resistance to heat changes. Both of these properties might be adversely affected by

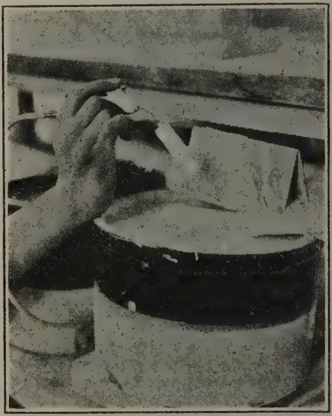

FIG. 7.—Applying the glaze slip to a core by dipping. This method was in use before the adoption of the present method of spraying.

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[1] This residue should be practically nil.

even a slight mistake in the proportions of the glaze ingredients.[1] If the tests prove normal the glaze slip in the storage tank is released for production.

(*b*) The second portion of the sample is tested for specific gravity and viscosity (Fig. 8). The former is determined by weighing 100 cubic centimeters of the slip, and the latter by the time taken for 210 cubic centimeters to flow through the orifice of a Bureau of Standards Viscosimeter.[2]

These two tests show whether or not a correction is needed. The specific gravity at this stage is usually between 1.460 and 1.465. With the specific gravity within these limits the viscosity of the regular slip should usually be 50 to 55 seconds.[3] If the viscosity is too low, an acid salt is used to increase it; if the viscosity is too high, additional water and, in extreme cases, a basic salt is added to lower it.

(6) As the glaze slip ages, the viscosity drops. The day before it is to be used another specific gravity and viscosity determination is taken to insure that the slip is normal. Additional correction can still be made at this stage. The next day the glaze slip is pumped through the circulation line to the spraying machines. While the slip is being sprayed, specific gravity and viscosity tests are taken several times during the day by the Production Division on samples drawn from the tank (Fig. 8).

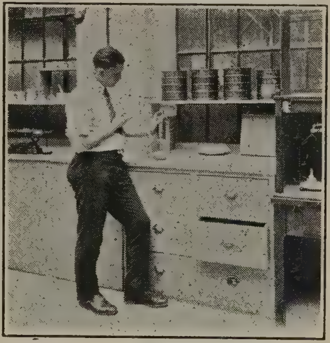

Fig. 8.—Laboratory of the production division where routine control tests of the glaze slip are made. The view shows the manner of taking the viscosity test. The balance at the right indicates the method of determining the specific gravity.

During the spraying the specific gravity of the slip usually lies within the limits 1.445 to 1.460. These correspond, respectively, to water contents of 50.4% to 49.3% in the slip. At the same time the viscosity usually is held between 42 and 50 seconds. These would seem rather wide limits for viscosity. Actually, however, other factors affecting the slip, such as the length of aging, the amount and kind of electrolytes, and the temperature, greatly narrow these limits for any given set of conditions.

(7) All of the data regarding a tank of glaze slip, date of milling, nature of the materials, results of the tests, amount of corrections, and comment as

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[1] F. H. Riddle and J. S. Laird, "The Control of Glaze Fit by Means of Tensile Test Specimens," *Jour. Amer. Ceram. Soc.*, **5** [8], 500(1922).

[2] A. V. Bleininger, "Use of Sodium Salts in the Purification of Clays and in the Casting Process," Bur. Stand., *Tech. Paper* **51.**

[3] Water has a viscosity of 25 seconds with this particular apparatus.

to its spraying qualities are all recorded for future reference. Accompanying each platform load of filled saggers is a ticket showing the number of the spraying machine and the date of spraying. If the ware should come from the kiln improperly glazed, it is a relatively easy matter to trace back and study the conditions surrounding each operation of preparation and spraying.

Notes on Preparation and Spraying of the Glaze Slip

This paper would hardly be complete without reference to some problems met in dealing with the glaze slip in production.

(1) Making the Glaze Slip

The glaze formulae used in this plant require a high raw clay content.[1]

Considerable difficulty has been caused by changes in the viscosity of the slip from mill to mill due to variations in the clays used. This is illustrated by examples shown in Table I. These three mills of slip received practically identical treatment. The differences in initial viscosity were due to variations in one of the clays used when taken from three separate shipments.

TABLE I

Tests taken		Specific gravity	Viscosity	Remarks
Time	Date	Glaze 745	Milled 7–4–1923	
3:00 P.M.	7–5	1.459	Would not flow through viscosimeter	
7:30 A.M.	7–9	1.458	$70\,^{1}/_{5}$ seconds	
Percentage of water in slip increased 0.14% by weight				
4:10 P.M.	7–10	1.456	$56\,^{2}/_{5}$ seconds	Spraying OK
		Glaze 745	Milled 8–31–1923	
8:00 A.M.	9–1	1.460	$88\,^{2}/_{5}$ seconds	
7:30 A.M.	9–5	1.461	53 seconds	
12:15 P.M.	9–6	1.462	$55\,^{1}/_{5}$ seconds	Spraying OK
		Glaze 745	Milled 9–30–1923	
12:15 P.M.	10–1	1.459	52 seconds	
10:45 A.M.	10–2	1.460	48 seconds	
Percentage of water in slip increased 0.31% by weight				
4:00 P.M.	10–4	1.456	45 seconds	Spraying OK

Such changes in the initial viscosity of the slip are probably due to differences in the amounts of soluble salts contained in the clays. These variations are best avoided by using three or more kinds of clay in making the slip, and by withdrawing each clay from a large supply which has been previously mixed as to render it practically homogeneous.[2]

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[1] Robert Twells, Jr., "The Field of Porcelain Glazes Maturing between Cones 17 and 20," *Jour. Amer. Ceram. Soc.*, **5** [7], 430(1922). "Further Studies of Porcelain Glazes Maturing at High Temperatures," *ibid.*, **5** [11], 1113(1923).

[2] Robert Twells, Jr., "Handling and Storing Raw Materials to Produce Uniformity in a Body," *Ibid.*, **7** [2], 82(1924).

The use of several kinds of clay in making the slip has been found desirable for other reasons. Laboratory experiments have shown that different types of clays when used singly give glaze slips of widely different viscosities. Generally speaking, a glaze slip made with a ball clay has a low viscosity, one made with a Florida kaolin has a medium viscosity, and one made with North Carolina kaolin has a high viscosity. By combining several clays in the porportions determined by experiment, it has been found possible to avoid the use of electrolytes to a large extent in preparing the slip. It is also desirable to use several clays to fit the slip coating properly to the body. Cracking, peeling or dusting of the dry slip can thus be avoided.

(2) Storing the Glaze Slip It formerly was the practice here to store the slip in one or two large storage tanks, each holding several mill charges. This method was never very successful. The slip in the tank was always an unknown mixture in different stages of aging. It usually would over-age before it could be used. The effect of aging a glaze slip is shown by Table II.

TABLE II

Tests taken		Specific gravity	Viscosity	Remarks
Time	Date	Glaze 787	Milled 1–11–1924	Tank No. 2
11:10 A.M.	1–12	1.465	100 seconds	
1:30 P.M.	1–14	1.465	52 seconds	
4:15 P.M.	1–15	1.466	46 seconds	
Percentage of water in slip increased 0.48% by weight				
7:30 A.M.	1–16	1.460	45 seconds	Spraying OK
1:00 P.M.	1–16	1.460	46 seconds	Spraying OK
4:15 P.M.	1–16	1.460	45 seconds	Spraying OK

As the slip is aged its viscosity falls. If it ages too long, an acid electrolyte must be used to raise the viscosity for spraying. This can be done, but usually it does not spray as well as a properly aged slip. On the other hand a newly made slip cannot be sprayed satisfactorily. This is no doubt due to the air bubbles which it contains. The correct length of aging the slip is probably from three to six days.

When the large slip storage tanks were abandoned for smaller ones, each holding one mill charge it was felt that this would solve many of the difficulties previously encountered. However, new troubles were met.

At first, after circulating through the supply pipes the slip was returned at the top instead of near the bottom of the storage tank. It thus fell with considerable force and carried a great many air bubbles into the slip remaining in the tank. For the same reason it was necessary to greatly reduce the agitation of the tanks and the speed of circulation of the slip in the supply line.

Another source of trouble was the lack of tops on the tanks. These were left uncovered to facilitate cleaning. It was soon found that the slip dried on the sides of the tank and kept dropping off. These pieces tended to clog the spraying nozzles. A more important effect on the lack of covers was on the temperature of the slip in the tanks. It was found very difficult to spray the slip when cold. When covers were put on the tanks, the heat, generated in the slip by friction, was held in the tanks, and the temperature became right for spraying. A typical record of the variations in the slip temperature are shown in Table III.

TABLE III

Tests taken		Specific gravity	Viscosity	Temperature	Remarks
Time	Date	Glaze 769	Tank No. 4	Milled 11–29–1923	
Room Temperature 79°F					
7:15 A.M.	11–30	1.444	41 seconds	80°F	
4:15 P.M.	11–30	1.446	39 seconds	81°F	
Slip Circulating in Supply Pipe					
7:15 A.M.	12–1	1.448	40 seconds	80°F	Spraying OK
11:10 A.M.	12–1	1.448	42 seconds	$89^{2}/_{10}$°F	Spraying OK
Slip Remained over Week End Merely Being Agitated in Tank					
7:30 A.M.	12–3	1.451	42 seconds	84°F	Spraying OK
Percentage of Water in Slip Increased 0.38% by Weight					
12:00 M.	12–3	...	....	88°F	Spraying OK
12:35 P.M.	12–3	1.446	$39^{2}/_{5}$ seconds	89°F	Spraying OK

As the slip circulates in the supply pipes its temperature rises rapidly. This results in a corresponding rise in the viscosity. In fact it is usually necessary as the slip warms up in circulating to add water to lower its viscosity in order to keep it spraying properly.

Other changes found necessary in practice were connections to admit compressed air and water to the slip circulation line for blowing and washing out at frequent intervals.

(3) Spraying the Glaze Slip

Obviously the slip must be atomized as uniformly as possible, or the nozzles could not be set to spray evenly to a given line on the cores. Thus the slip must flow evenly through a small orifice—not in lumps or clots. The air pressure for atomizing must be kept steady and at a definite pressure.

The guards must be easily adjusted and properly designed to assist in warding the spray off the portions to be left unglazed.

Direct connection of the nozzles with the circulation line was found undesirable because the pressure in the line is too high and irregular. A hopper is now used on each spraying machine to hold a small supply of slip. It was found necessary to install a combined agitator and lawn in these hoppers, in order to keep the slip uniform and free from lumps.

If the lines between the sprayed and unsprayed surfaces are not at the same points on successive cores, the slip may be either too light or too heavy. If the slip tends to settle in the hoppers, if the unsprayed surfaces show a heavy coating of slip dust, and if the slip coating on the sprayed surfaces is not smooth and firm but is rough and spongy, the slip is too heavy, *i. e.*, it contains either too little water, too much acid electrolyte, or both. If the spray beads up irregularly on the core, and flows somewhat raggedly over the unsprayed surfaces, the slip is too light, *i. e.*, it contains either too much water, too much alkaline electrolyte or both. Where the equipment and operating conditions are normal, and the specific gravity of the slip is held within limits, it is usually safe to assume that trouble in spraying is due to the nature and amount of the soluble materials in the slip. Attempts to correct the spraying qualities of the slip with electrolyte while it is being used, has seldom been successful. This seems to make the slip spray even more irregularly for a time. The practice which has given the best results has been to mill the slip slightly heavier than required, and then to water it down gradually until it sprays satisfactorily. This makes use of the soluble salts already in the materials and avoids to a large extent further additions of electrolytes.

Summary

The rather difficult operation of spraying spark-plug cores has been made comparatively easy by the following factors:

(1) The design and construction of better equipment.

(2) More careful control of composition and homogeneity of the raw materials.

(3) Use of such a mixture of clays in making the glaze slip as to produce naturally the viscosity desired without further additions of electrolytes.

(4) Improved milling and aging of the slip.

(5) Handling the slip in batches, each consisting of one mill charge.

(6) Frequent specific gravity and viscosity tests of the slip as it is being aged and sprayed.

DETROIT, MICH.

Discussion

MR. FRITZ: Your viscosity is not always the same for spraying, is it?

MR. TWELLS: No. The specific gravity may be held fairly constant, but the viscosity has to be varied to meet new conditions as they arise. Fortunately, however, in every-day practice where the atmospheric conditions do not differ widely and there has been no change in raw materials, it is possible to hold the viscosity within fairly close limits and be sure of good results.

Mr. McAfee: Are the viscosity determinations made under standard temperature conditions, or are the conditions constant enough in the plant? If the latter is the case, would you think it necessary, in a plant where the temperature varies considerably, to have a calibration with reference to temperature?

Mr. Twells: We do not make our viscosity tests at a standard room temperature, and for our requirements we hardly think that it is necessary. We are interested in measuring the viscosity of the slip at its temperature in the tank, not at the room temperature. Consequently we take the slip from the tank and test it at once, before it has a chance to cool.

Mr. Fritz: We maintain a somewhat similar control of the glaze in our plant. We have found that it is necessary to keep the viscosity within certain limits and in doing this, the weight may vary considerably, since we do not always necessarily get the same weight for the same viscosity. We know, however, that if the viscosity is right, the glaze is fit for use, regardless of the weight, and our control is based entirely on this principle.

The variation in the relation of viscosity to weight, besides being due to the controllable factor of temperature and length of blunging is also dependent on the type of clay used and variations in any one type of clay. We cannot predict the latter, and adjustment is more for this factor after the clay has been run into the storage cistern from the mixing mill. It is often not necessary to make any adjustment whatever, for we have gone along for several weeks, with no change in the viscosity of the glaze, as it came from the mill. However, by checking each batch, the system is fool proof, and we have no difficulty in maintaining uniform glaze coatings.

THE PROBLEM OF HEAT ECONOMY IN THE CERAMIC INDUSTRY—II[1]

BY WILLI COHN

Results of the Experiments

A. Tests with the Calorimeter

Thanks to the kindness of Professor Dr. Bauer, to whom acknowledgment is here made, it was possible to use the same test materials which had already been used by Heyn, Bauer and Wetzel.[2] Numerous kinds of fire clays had been investigated by them, both as to thermal conductivity and as to specific heat. These investigations were made at temperatures up to 1200°C. They had determined specific heat in the usual way calorimetrically by the method of mixtures.

As reference substance we selected fired fire-clay body "4." From the values of specific heat under various temperatures, as indicated by Heyn, etc., we calculated the *q-t* curve; compare Fig. 23, where also the values of the mean and the true specific heats, c_m and c_w, are given. This figure also shows the graphic determination of c_w and c_m from a given initial temperature.

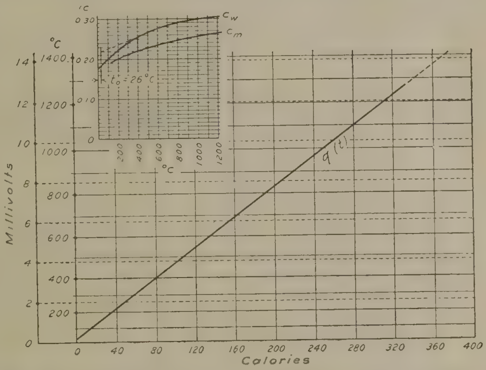

FIG. 23.—Fired fire-clay body "4" used by Heyn, Bauer and Wetzel.

In these tests the readings of the temperature were in millivolts; consequently temperature on the *q-t* curve is also indicated in millivolts. A curve of this sort is given in Fig. 23*a*. It will be seen that it is not a straight line, consequently the standard measure of temperature (°C) in Fig. 23 is not a *uniform* one. The curve of specific heat in Fig. 23 shows that

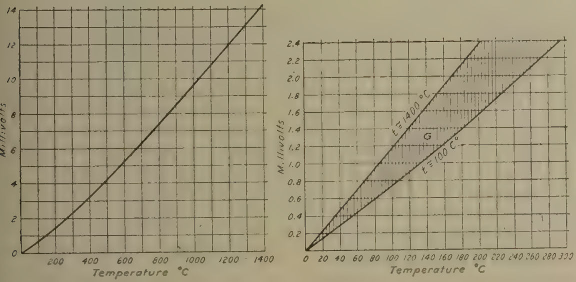

FIG. 23*a*.

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[1] For Part I of this paper see *Jour. Amer. Ceram. Soc.*, **7** [5], 359(1924).

[2] Heyn, Bauer and Wetzel, "Untersuchungen über die Wärmeleitfähigkeit feuerfester Baustoffe," Mitteil. aus d. Königl. Materialprüfungsamt, 1914, 213.

specific heat is variable with temperature; hence it is to be expected that the q-t curve calculated on the basis of specific heat will also result in a curved line.

On the chart which indicates temperature in millivolts both curvatures accidentally cancel each other so that the q-t curve for this substance appears as an almost straight line.

B. Preparing the Curve Chart

Fig. 24 has been made for the reference material body "4." By reason of the great exactness of the measurements—obtainable by the differential method employed—it is possible to indicate G in proportion of 5:1 as compared with the furnace temperature.

During the experiments G was measured in millivolts.

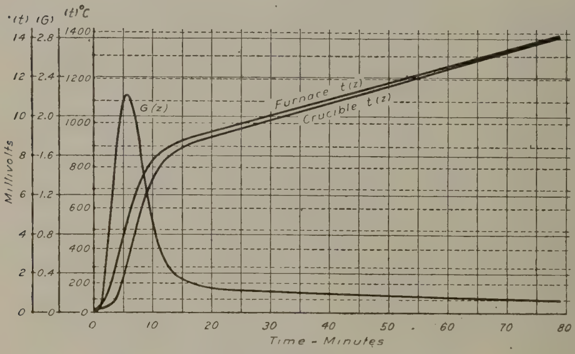

FIG. 24.—Fired fire-clay body "4".

In contradistinction to temperature t which was also determined in millivolts, it is not feasible to read the extent of temperature differences between furnace wall and crucible directly from the calibration of the thermoelements in terms of degrees. Let us suppose the furnace wall has a temperature of 375 °C corresponding to 3.0 millivolts, and the substance has 263 °C, corresponding to 2.0 millivolts; the difference then is 112 °C, corresponding to a difference in the reading of 1.0 millivolt. If the temperature of the furnace wall is 1292 °C, corresponding to 13.0 millivolts, and the substance is 1207 °C, corresponding to 12.0 millivolts, the difference in temperature would then be 85 °C, while the difference in reading, as in the preceding case, is 1.0 millivolt.

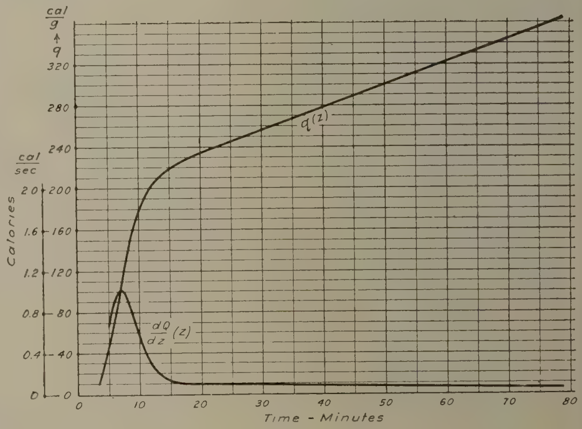

FIG. 25.—Q = two grams.

Fig. 23*a* gives a shaded area within which the values of G, expressed in °C are located, corresponding to a definite value of G, expressed in millivolts.

From this test resulted directly the t-z curve for the furnace, as well as the G-curve. From these two we obtained, by subtraction, the t-(z) curve for the crucible material. The q-(t) curve, together with the t-(z) curve, was combined into the q-(z) curve. (In Fig. 25.)

The curve, considered as a *furnace characteristic* is *independent* of the nature of the test material; it represents the *total* flow of heat used for G and t. The quantity of heat q refers to 1 g. of the substance and is measured in cal./g. Our test arrangements provided for 2 g. of the substance.

The amount of heat requisite for heating 2 g. of substance, which was actually measured during our test, is hereafter indicated as Q. The following relation thus exists between Q and q:

$$Q = 2q$$

In this connection q is measured in cal./g; Q in cal., since "2" represents the weight in grams.

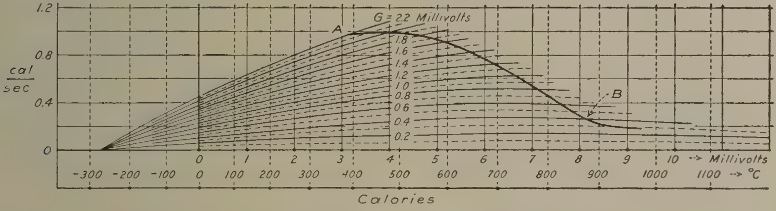

FIG. 26.—Furnace characteristic.

The differentiation of the q-(z) curve (carried out according to Sanden[1]) and the doubling of its values gives us the $\frac{dQ}{dz}(z)$ curve needed for preparing the curve chart; this is also indicated in Fig. 25.

Numerous temperature-time curves were made with the reference material body "4," and then calculated in the manner described. Next all $\frac{dQ}{dz}(z)$ curves with the aid of the $t(z)$ curves were drawn as $\frac{dQ}{dz}(t)$ curves. By combining those points which had a like G we obtained the furnace characteristic shown in Fig. 26.

We have drawn into the furnace characteristic, as an example, the values of the curve for fire-clay body "4" in Figs. 24 and 25 (Curve A-B, Fig. 26, for the sake of clearness a part only of the descending branch of the curve has been indicated).

The checking up of the curve chart was done by comparing the results obtained with known values; further details are referred to under quartz, cristobalite and fired fire-clay, which had already been tested by Heyn, Bauer and Wetzel.[1]

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[1] H. v. Sanden, "Praktische Mathematik," Berlin, Urban (1920).

C. Determining the *q-t* Curves

To determine the *q-t* curves from the furnace characteristic we selected Zettlitz kaolin for the experiment; the results appear in Figs. 27 to 29.

Several temperature-time curves (at varying rates of speed during heating) were made for this material. Fig. 27 represents such a curve on a small scale. With the aid of the furnace characteristic we then developed the $\frac{dQ}{dz} - (z)$ curves.

The determination of the *q-z* curve was made on the basis of the following:

$$q = \int dq = \int \left(\frac{dq}{dz}\right) dz = {}^1/_2 \int \left(\frac{dQ}{dz}\right) dz$$

The two last-named curves have been drawn in Fig. 28. The integration constant, however, has not been considered; it results on the supposition that at the initial temperature of the experiment $q = 0$. In other respects the integration constant has no influence on the determination of c_w, since $c_w = dq/dt$ is independent of the absolute value of the function $q(t)$.

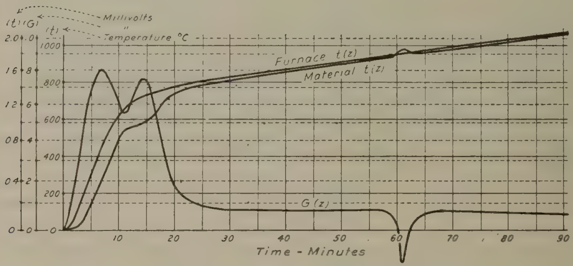

FIG. 27.

Combining the *q-z* and the *t-z* curves gives the desired *q-t* curve from which the desired values can be determined directly, according to Fig. 29.

Zettlitz Kaolin

Temperature-time curve of Zettlitz kaolin (clay substance 98.5%) shows several reactions. These appear particularly sharp on the *G-z* curve by reason of the considerably enlarged scale (in Fig. 27). The same reactions may also be clearly seen on the *q-t* curve.

The heating curves show that the degree of temperature at which a certain reaction takes place is independent of the rate of heating. All temperature-time curves have the same *q-t* curves. The *q-t* curves determined from various temperature-time curves varied at the most by ±3%.

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[1] *Loc. cit.*

1. Endothermal Reaction

On the temperature-time curve there appears clearly the splitting off of chemically combined water. This attained its maximum at about 575°C. The heat consumption of this endothermal reaction, on the q-t curve, shows 91.8 ± 3 cal./g.

Fig. 29 shows how this value has been determined. Such endothermal reactions scarcely ever present exactly horizontal curve sections hence the curve lines above and below the reaction in question must be extrapolated as is done in our figures.

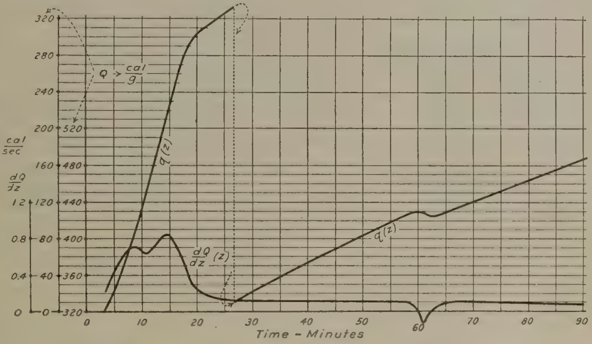

FIG. 28.—Development of q-t curves, unfired Zettlitz kaolin $Q = 2$ g.

2. Exothermal Reaction

An exothermal process appears at about 950°C, the chemical significance of which is not yet fully clear. It is now generally assumed that a combination of Al_2O_3 and amorphous SiO_2 is involved. On the q-t curve up to this point the temperature rises fairly regularly with the inducted heat. Then appears a sudden rise in temperature of nearly 50°C as a result of the exothermal reaction in the mass. The loss of heat then becomes so considerable that q declines and the temperature falls. After that again begins an increase in temperature with the inducted heat. In this manner originates the loop on the q-t curve.

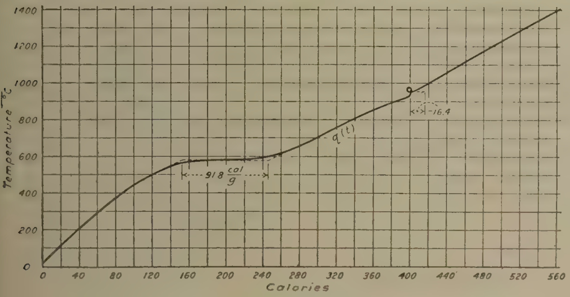

FIG. 29.—q-t curve for unfired Zettlitz kaolin.

The extent of the exothermal reaction is obtained by extrapolation of the lower curve sections up to that point of the temperature from which the rise is steadily upwards. See Fig. 29. The extent of the heat changes so occurring is: -16.4 ± 0.5 cal./g.

3. Further Reactions

Before the exothermal process the G-z curve shows a rise similar to that in an endothermal process. During this the temperature of the substance remains below that of the furnace. In consequence G is increased. From about 650°C on to the temperature of the exothermal process, the q-t curve declines more than is expected from the remaining curve sections.

It seems that a gradual endothermal process takes place which may, in part, be overlapped by the exothermal process. At any rate it is noticeable that at this temperature the disintegration of the kaolinite molecule has proceeded to its fullest extent. This appears also from the high solubility of the clay substance in hydrochloric acid at this temperature.

4. Consumption of Heat

The consumption of heat at a given temperature, of vital concern for the industry, can be determined directly from the q-t curve. In order to heat 1 g. of Zettlitz kaolin from an initial temperature of 20°C up to the following temperatures there is required:[1]

Temp. °C	100	200	300	400	500	600	700	800	900	1000	1100	1200	1300	1400
Cal.	16.1	36.7	59.6	85.7	119.4	240.5	292.5	332.6	385.9	420.4	454.8	488.8	524.6	560.3

5. Specific Heat

From the values of the q-t curve the mean specific heat is found according to the formula $q = c_m(t-t_0)$. For an initial temperature of $t_0 = 20$°C we find from the above values:[1]

Temp. °C	100	200	300	400	500
c_m	0.201	0.203	0.213	0.226	0.249

As soon as the endothermal reaction occurs, the mean (and with it the true) specific heat assumes wholly abnormal values. It does not appear necessary to indicate them. It is sufficient to know the expenditure of heat necessary to attain a certain temperature; this expenditure is indicated above. According to Fig. 23 one may graphically show how to determine actual specific heat.[1]

China Clay

As a second representative of clay materials we tested china clay containing 97.5% of clay substance. The reactions occurring on the temperature-time curve as well as those on the temperature-heat curve were the same as for Zettlitz kaolin and differ but slightly from the latter.

1. Endothermal Reaction. This reaction appeared most noticeably at about 575°C. It amounts to 92.6 ± 3 cal./g.

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[1] These data are repeated, together with similar data for all the other substances investigated, in Tables I and II.

2. Exothermal Reaction. At a temperature of 950°C the *q-t* curve showed the same loop as indicated for Zettlitz kaolin. The value determined was -16.0 ± 0.5 cal./*g*.

The consumption of heat and the specific heat will be found in Tables I and II.

From the numerical values it appeared that the behavior of china clay during heating not only qualitatively but also quantitatively coincided to a high degree with that of Zettlitz kaolin. From this we may conclude that the behavior of other kaolins will yield values which will deviate but slightly from the values here given.

Pure Clay Substance

By recalculating the values found for Zettlitz kaolin and china clay over to a pure clay substance we obtained the following mean values:

1. Endothermal Reaction. For the splitting off of water in chemical combination in pure (100%) clay substance, is required: 94.0 ± 3 cal./*g*.

2. Exothermal Reaction. The amount of heat set free by the reaction at about 950°C is -16.5 ± 0.5 cal./*g*.

These values were made the basis for the subsequent calculations of heat-changes of ceramic materials.

Previous Investigations

Mellor and Holdcroft[1] investigated the constitution of the kaolin molecule, and, among other things, also made heating curves. They made use of the following testing-device:

The test-substance was contained in a crucible which had been placed into another crucible; the space between the two having been filled with sand. The two were then heated over a Bunsen burner. With the aid of a thermoelement in the substance and another in the sand filling—to serve for checking purposes—the temperature-time curves were then made.

By some graphic method, not indicated, they determined values for heat-changes occurring during the heating of kaolinite. They designated them as "rough approximations not without grave errors."

They obtained the following results: For the endothermal process at 575°C: 42 cal./*g*; for the exothermal process at 950°C: -21.5 cal./*g*. Because of the testing device, these values can scarcely lay claim to accuracy.

D. Tschernobaeff[2] by heating in a bomb obtained 112 cal./*g*. This value, however, includes the values for all the reactions which occur be-

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[1] Mellor and Holdcroft, *loc. cit.*

[2] *Rev. Met.*, 729, 1905.

TABLE I

Material	Heat needed in gram-calories to heat materials from 20°C to														Quantity of heat in gram-calories		
	100	200	300	400	500	600	700	800	900	1000	1100	1200	1300	1400°C	Endothermal reaction	Exothermal reaction	Heat of conversion
Zettlitz kaolin	16.1	36.7	59.6	85.7	119.4	240.5	292.5	332.6	385.9	420.4	454.8	488.8	524.6	560.3	91.8	−16.4	...
China clay	16.0	36.4	59.5	85.8	118.9	241.5	297.8	330.6	386.6	421.1	454.4	490.8	526.1	561.9	92.6	−16.0	...
Amorphous clay	15.9	36.3	60.4	86.1	115.1	144.8	175.5	209.3	244.3	298.9	...	...	...	...	....	....	...
Artificial corundum	16.3	37.9	62.4	87.7	116.2	145.2	176.1	212.2	252.3	297.6	...	...	...	...	....	....	...
Sillimanite, artificial	12.9	28.9	45.6	63.4	81.5	100.2	118.2	135.6	153.2	171.5	211.3	235.3	259.4	282.4	....	−19.9	...
Feldspar	12.9	29.1	47.1	67.8	91.7	116.7	143.4	172.1	201.9	240.5	281.2	309.7	...	...	....	....	...
Norwegian quartz	15.2	37.1	60.9	86.5	114.9	148.3	174.7	202.7	231.3	262.0	...	...	...	...	....	....	4.2
Rose quartz	15.2	36.8	60.2	85.9	114.8	148.1	174.3	202.3	231.0	261.7	...	...	...	...	....	....	4.1
Sand from Hohenbocka	15.2	36.8	60.1	84.5	112.0	145.2	173.2	201.0	230.5	261.5	...	...	...	...	....	....	4.1
Amorphous silicic acid	17.1	40.3	66.0	93.2	122.0	151.0	180.1	209.5	239.5	272.0	...	...	...	...	....	....	...
Cristobalite	15.5	38.0	66.2	90.3	117.1	144.0	170.3	199.7	228.7	259.9	...	...	...	...	....	....	6.0
Chalcedony	13.3	31.0	48.8	67.4	88.8	109.7	131.1	154.1	178.4	206.0	236.2	...	...	...	....	....	...
Porcelain, green	14.8	33.6	55.2	80.9	109.0	192.8	220.1	248.4	285.6	330.8	379.5	428.4	477.5	527.7	53.1	− 8.8	...
Porcelain, fired	15.1	35.1	57.0	80.2	106.8	134.6	166.7	205.8	252.9	307.8	363.9	...	...	...	....	....	...
Porcelain glaze, green	13.6	31.3	51.2	73.2	100.0	143.1	162.2	202.4	244.4	274.8	313.8	352.9	393.3	403.0	16.4	−12.3	...
Porcelain glaze, fired	14.3	32.6	52.9	74.7	95.8	117.0	159.0	164.0	192.1	226.3	265.0	...	...	...	....	....	...
Stoneware, green	14.5	33.0	53.8	76.1	103.3	168.5	196.0	218.4	247.0	283.8	335.4	387.6	440.7	...	48.9	− 7.9	...
Stoneware, fired	14.9	34.6	56.9	80.4	106.6	124.8	187.2	193.7	259.0	300.6	351.1	...	...	...	1.7	....	...
Chamotte, green	15.3	34.9	56.2	80.0	111.8	201.4	225.6	242.8	283.3	336.1	394.1	452.6	512.9	571.7	81.2	−13.8	...
Chamotte, fired	15.8	36.4	59.5	83.6	110.6	138.2	166.2	195.6	228.3	270.7	311.3	...	...	...	....	....	...
Chamotte "BC," fired	15.9	38.7	63.4	88.9	114.6	140.7	168.6	196.2	227.6	256.3	286.4	315.0	347.1	379.0	....	....	...
Halle clay, green	15.1	35.2	59.0	84.9	118.2	202.7	234.3	258.3	284.1	337.5	387.4	436.4	...	...	62.2	−11.9	...

TABLE II

Material	Average specific heat in mean calories between 20°C and													
	100	200	300	400	500	600	700	800	900	1000	1100	1200	1300	1400°C
Zettlitz kaolin	0.201	0.203	0.213	0.226	0.249	*	...	...	...	...	...	...	...	...
China clay	0.200	0.202	0.213	0.226	0.248	*	...	...	...	...	...	...	...	...
Amorphous clay	0.199	0.202	0.216	0.227	0.240	0.250	0.258	0.268	0.278	0.305	...	...	...	...
Artificial corundum	0.203	0.211	0.223	0.231	0.242	0.251	0.259	0.272	0.287	0.304	...	...	...	...
Sillimanite, artificial	0.161	0.161	0.163	0.167	0.170	0.173	0.174	0.175	*	...	...	...	...	...
Feldspar	0.161	0.162	0.168	0.179	0.191	0.202	0.211	0.222	0.229	0.246	0.260	0.262	...	...
Norwegian quartz	0.190	0.206	0.217	0.228	0.239	0.256	0.257	0.260	0.263	0.267	...	...	...	...
Rose quartz	0.190	0.205	0.215	0.226	0.239	0.256	0.257	0.259	0.262	0.267	...	...	...	...
Sand from Hohenbocka	0.190	0.205	0.214	0.223	0.233	0.251	0.254	0.257	0.262	0.267	...	...	...	...
Amorphous silicic acid	0.214	0.224	0.236	0.246	0.254	0.260	0.265	0.269	0.272	0.277	...	...	...	...
Cristobalite	0.194	0.212	0.237	0.238	0.244	0.248	0.252	0.257	0.261	0.266	...	...	...	...
Chalcedony	0.167	0.172	0.175	0.177	0.185	0.189	0.193	0.198	0.203	0.210	0.218	...	...	...
Porcelain, green	0.185	0.187	0.197	0.213	0.228	*	...	...	...	...	...	...	...	...
Porcelain, fired	0.189	0.195	0.203	0.212	0.222	0.232	0.245	0.264	0.287	0.304	0.337	...	...	...
Porcelain glaze, green	0.170	0.174	0.183	0.193	0.208	*	...	...	...	...	...	...	...	...
Porcelain glaze, fired	0.179	0.181	0.189	0.197	0.199	0.202	0.204	0.211	0.218	0.230	0.245	...	...	...
Stoneware, green	0.181	0.183	0.192	0.201	0.215	*	...	...	...	...	...	...	...	...
Stoneware, fired	0.186	0.192	0.203	0.212	0.223	0.234	0.275	0.286	0.296	0.307	0.324	...	...	...
Halle clay, green	0.189	0.195	0.211	0.223	0.247	*	...	...	...	...	...	...	...	...
Chamotte, green	0.191	0.194	0.201	0.211	0.232	*	...	...	...	...	...	...	...	...
Chamotte, fired	0.197	0.202	0.213	0.220	0.231	0.238	0.244	0.251	0.230	0.277	0.288	...	...	...
Chamotte "BC" fired	0.199	0.215	0.227	0.233	0.239	0.243	0.248	0.252	0.258	0.261	0.264	0.267	0.271	0.274

*The quantities of heat necessary to attain higher temperatures may be obtained from Table I.

tween 20° and 1300°C. Consequently no conclusions can be drawn from this as to the values for the several reactions.

Knote[1] in a brief article, reports some tests for determining the specific heat of clays by means of an Emerson calorimeter. (Mixing method.) The clays tested by him were of the following composition (unfortunately he gives only the total analysis): SiO_2 53.30%, Al_2O_3 30.88, Fe_2O_3 0.71, CaO 0.50, MgO 0.08, TiO_2 2.21, alkalies 0.12, loss on ignition 12.24. The values of specific heat found by this author are: (between 22° and 150°C), raw 0.237, calcined at 650°C 0.204, at 1050°C 0.200.

In these values it is striking that in contrast with all other measurements of specific heat of bodies of similar composition, and especially of minerals,[2] the specific heat of a modification stable at a high temperature is less than that of a modification stable at a lower temperature.

From the values reported in the course of the present investigation, and compiled in Table II, it can be seen that the materials in use in ceramics have a higher specific heat in their fired state than in the unfired.

This behavior is paralleled by Van't Hoff-Thompson's law according to which the modification of a body, stable at high temperature, has a higher specific heat than the modification which is stable at low temperature.

Amorphous Alumina

Amorphous alumina was obtained by heating precipitated aluminum hydrate. The heating curve of this substance—in contradistinction to amorphous alumina obtained from aluminum nitrate—showed no reactions. Also the *q-t* curve showed no reactions. The values determined from this curve are given in Tables I and II.

The values obtained below the temperature of dehydration coincide closely with the results obtained with Zettlitz kaolin and china clay.

Artificial Corundum

With artificial corundum (molten alumina) no reactions appeared on the heating curve. The curves ran absolutely uniform and showed the values given in Tables I and II. These values, in agreement with the previously mentioned principle, were higher than those of unfired material.

Sillimanite

Sillimanite $Al_2O_3.SiO_2$ (amorphous) prepared in an electric arc[3] yielded the following results during heating (Fig. 30).

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[1] Knote, "Note on the Specific Heat of Clay," *Trans. Amer. Ceram. Soc.* (1912); Ref. *Silikat-Zeitschrift* (1914).

[2] W. P. White, "Specific Heat Determination at Higher Temperatures," *Am. J. Sci.*, **47** (1919); Ref. *Phys. Ber.*, **13** (1920).

[3] Kindly furnished me by Mr. Blei, a student in chemistry at the Chemo-Technical Experiment Station of the Government Porcelain Factory at Berlin.

1. Exothermal Reaction. At about 950°C an exothermal reaction occurred, the cause of which cannot be stated as yet. The amount of heat liberated was −19.9 ± 0.6 cal./g.

2. Other Reactions. In agreement with the formula given above, no splitting off of water in chemical combination took place. On the other hand, there was a noticeable gradually continuing endothermal process below the exothermal reaction.

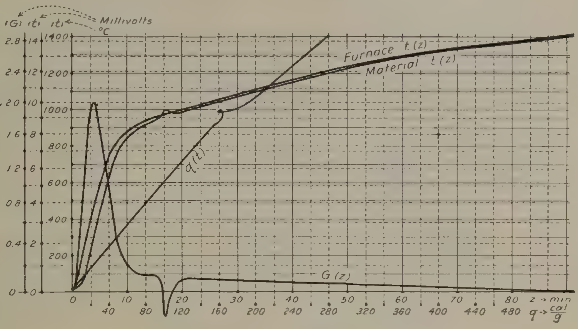

Fig. 30.—Sillimanite.

The steep rise of the *q-t* curve in itself points to the fact that the specific heat is unusually low. The data are included in Tables I and II.

Feldspar

The curves obtained for very pure Norwegian potash feldspar ran uniform throughout showing no reactions whatever. From about 1100°C the *q-t* curve is quite flat. This means an increase of the apparent specific heat; probably due to an incipient fusion. This, according to Nacken[1] sets in at about 1200°C.

The several results are included in Tables I and II.

Quartz

In order to get a survey of the various modifications of quartz as they occur in nature, the following materials were submitted to tests: (1) Crystalline silica (Norwegian quartz, rose quartz, Hohenbocka sand); (2) amorphous silica; (3) cristobalite; (4) chalcedony.

Norwegian Quartz The temperature-time curve clearly showed the transformation of α-quartz into β-quartz occurring at 575°C. This was clearly observed on a curve made at a slow rate of heating. The temperature-time curves required for the higher temperatures and taken with a greater speed in heating, of course, also show this reaction.

The *q-t* curves determined from the *t-z* curves agreed well with each other, in consonance with the other test-materials. Fig. 31 shows a *t-z* curve made at a slow rate of heating, as well as a portion of a curve made at greater speed. It also shows the *q-t* curve developed from these.

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[1] R. Nacken, *loc. cit.*

The transformation of quartz to tridymite cannot be observed on these curves because this transformation is so extremely slow.

The following values resulted in detail:

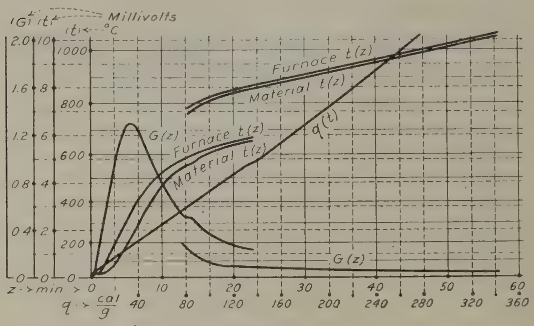

Fig. 31.—Norwegian quartz.

1. Heat of Transformation. The transformation of α-quartz into β-quartz occurring at 575°C is an endothermal reaction. The value of this reaction determined from the *q-t* curve is 4.2 ± 0.2 cal./*g*. The consumption of heat and the specific heat are given in Tables I and II.

Rose Quartz

In order to study the behavior of crystalline silica in another substance we tested some very pure rose quartz which had been placed at our disposal by Professor Tannhäuser. It reacted very much like Norwegian quartz.

Hohenbocka Sand

This has a silicon dioxide content of 99.95%. It finds extensive use in ceramic industries. The heating curve showed the course typical for all kinds of quartz.

From the numerical values given in Tables I and II it can be seen that the results from these three crystalline silicas show a fairly close agreement. In the following we shall take up the results which have been obtained previously.

Previous Tests

1. Heat of Transformation

The only reference to heat-changes in the transformation of quartz is by White and is referred to by Wright and Larsen.[1] His value of this transformation heat is 4.3 ± 1 cal./*g*.

This agrees well with our results although obtained by a graphic method.

From the values of specific heat established by White we can graphically determine the heat changes at 575°C with the aid of the formula $q = c_m(t-t_0)$. Where the specific heat is known, it is possible to calculate the quantity of heat at the various temperatures. If we employ *q* as a function of *t*, the curve resulting will be uniform, showing a break only at a temperature of 575°C. By extrapolating the curve below and above the transformation temperature any heat change occurring during the reaction is determined.

---

[1] F. E. Wright and E. S. Larsen, "Quarz als geologisches Thermometer," *Am. J. Sci.*, **27** (1909); *Z. f. anorg. Chem.*, **68** (1910).

2. Specific Heat A large number of investigations have been made. White[1] investigated up to high temperatures by the method of mixtures. The values determined by him (mean specific heat between 0°C and higher temperatures) are as follows:

Temp. °C	100	300	500	700	900	1100
c_m	0.1868	0.2168	0.2381	0.2543	0.2595	0.2684

These values coincide very well with those found by us.

Schulz[2] also used a water calorimeter. The values found by him (mean specific heat between 20°C and higher temperatures) are as follows:

Temp. °C	100	250	410
c_m	0.1871	0.2086	0.2253

These figures also agree well with ours.

See Schulz[2] for a condensed survey of experimental results with quartz by various investigators.

After having determined the values for crystalline silicon dioxide we studied the behavior of amorphous silicon dioxide during heating.

Amorphous Silicon Dioxide

By moderate ignition of silicic acid at about 700°C amorphous silica was prepared. The heating curves obtained show a uniform course throughout. No reactions of any sort were noticeable. The results are contained in Tables I and II.

Cristobalite

Cristobalite prepared from "flint" showed very clearly, under sufficiently slow heating, the transformation of the α to the β modification. Further transformations could not be observed.

The transformation of α cristobalite into β cristobalite occurred at 235°C. From the q-t curve the consumption of heat for the endothermal process was 6.0 ± 0.2 cal./g. The consumption of heat and the specific heat are given in Tables I and II.

Cristobalite being the modification which is stable at the higher temperature has a specific heat greater than crystalline silica.

The mean specific heat of cristobalite found by White by calorimetric tests and the method of mixtures at different temperatures from 0°C were:

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[1] W. P. White, *loc. cit.*

[2] K. Schulz, "Über die mittlere spezifische Wärme von Quarz und Quarzglas in drei verschiedenen Temperaturbereichen," *Centralbl. f. Min. usw.* (1912).

Temp. °C	100	300	500	700	900	1100	1300	1400
c_m	0.1882	0.2332	0.2425	0.2508	0.2568	0.2625	0.2662	0.2680

These values show good agreement with the results we have obtained.

Chalcedony

A large number of heating curves were made at various speeds of heating. In agreement with Fenner[1] there appeared no reaction whatever on these curves. Laschenko, whose findings are referred to by Rieke,[2] claimed to have found a heat-change in chalcedony at 230°C. Such a reaction in no case appeared during our tests.

The temperature-time curve and the temperature-heat curve appeared uniform throughout and showed values given in Tables I and II.

(To be continued)

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[1] C. N. Fenner, "Die Stabilitätsbeziehungen der Kieselsäuremineralien," *Z. f. anorg. Chem.*, **85** (1914).

[2] R. Rieke, "Neure Fortschritte auf dem Gebeit der keramischen Chemie," *Fortschr. d. Ch. usw.*, **6** (1912).

GLOSS GLAZES AND INDIAN DESIGNS ON NORTH DAKOTA POTTERY[1]

BY MARGARET CABLE[2]

Introduction

The problem outlined below was carried out by students in the Ceramic Department of the University of North Dakota. The students to whom this particular problem was presented derived much real pleasure and profit, not only in the actual execution and possession of the pieces made, but also in the study of Indian pottery necessary in their search for suitable design material.

The problem was to make and decorate a suitable form with a design more or less typical of Indian pottery, the design itself to be carried out in colored gloss glazes while the warm background tone of the whole was to be accomplished by a thin spray of glaze of harmonious color.

No attempt was made to merely imitate Indian pottery or to make use of Indian methods or processes of decoration. Colors generally foreign to these wares such as green and blue were freely used, the idea being simply that the bold beautiful patterns seen on many of the best examples of Indian pottery afforded a fruitful study and presented a rich field of design which could be adapted and translated for modern ceramic work.

The floating on or inlaying of colored glazes is, of course, an ancient process, nor is there anything new in the use of Indian motifs for pottery decoration, but the two ideas have not been combined with just the same results as were obtained in this particular instance.

Source of Design Material

The inspiration and design material was drawn entirely from books. The Annual Report of the Smithsonian Institution for the years 1901 and 1902 proved very helpful, as did the Reports of the Bureau of Ethnology for the years 1882–83 and 1895–96. These reports, especially the latter, contain many beautiful colored plates and much interesting and instructive descriptive matter. There are available, of course, many magazine articles and books on primitive and Indian pottery and basketry.

After the student had become familiar with the contents of these volumes and had absorbed something of the rhythm, the boldness and the beauty of Indian design, the actual work of carrying out the design on the piece itself was begun.

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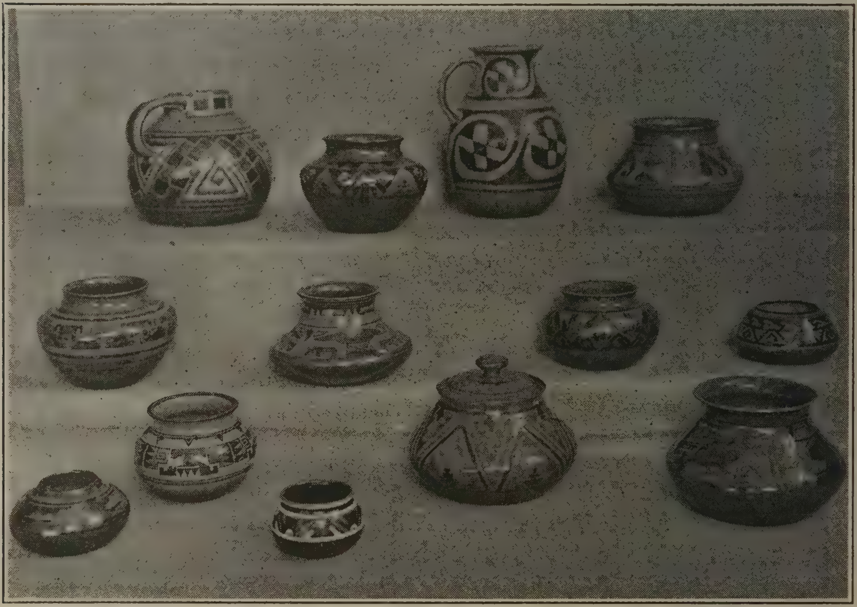
[1] Presented at the Atlantic City Meeting, Feb., 1924 (Art Division).

[2] Assistant Professor of Ceramics, University of North Dakota, Grand Forks, North Dakota.

Selection of Form

As the aim was not to copy Indian pottery, but to use modern methods and glazes in the production of a pleasing and artistic product with a flavor of Indian about it, we did not feel that it was essential to adhere entirely to typical Indian shapes which are apt to be rather too rounding on the bottom for the present day comfort and stability. We selected, rather in the main, low full curved bowls with fairly broad substantial bases.

The forms themselves may be built, thrown or cast at the convenience of the worker. We used the latter method for the reason that there had been made previously by this group of students several molds, the shapes of which were well adapted to this particular need.



Body

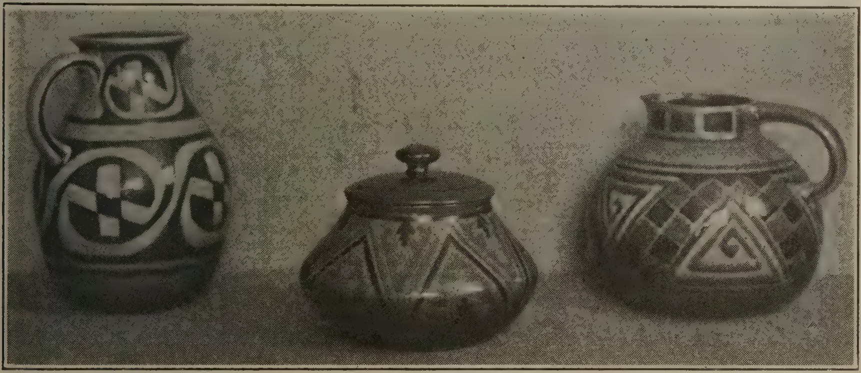
A light colored body is essential if the transparent gloss glazes given later are employed. Entirely different color effects would result if these glazes were applied to a red body, for example. A porous body of a light cream color was used in these pieces, as the high grade potter's clays of North Dakota, on which our research work is being done in the Ceramic Department of the University, burn to an ivory or light cream color.

Outlining Design

After the vessels were cast, dressed down and dried, the designs, carefully drawn and fitted to the space, were traced upon the green ware. A suitable underglaze color, preferably dark brown or black was then mixed with a little dissolved gum arabic and water to a consistency which flowed easily from the brush, and the outline was painted in with the underglaze color using a fairly bold, broad brush line. The pots were then biscuited and the work of filling in the various units of the design with colored gloss glazes was begun.

Selection of Colors

It seemed more in keeping with the style and the type of decoration to limit the colors used in the design itself to two or possibly three colors, as it was felt that, inasmuch as the designs were bold and simple, they should be carried out with a corresponding simplicity of color arrangement. Blue and brown were combined with perhaps a touch of green or brownish black and green, with a suggestion of red.



The background color decided upon, a warm orange brown and buff, was practically the same for all the pieces and was obtained by spraying on with the air brush a thin glaze coat of these two colors which permitted the light cream clay body to show through the orange brown, giving thereby a suggestion of the shading and warmth of real Indian wares.

The Glaze

The following table gives the composition of the glaze. Gloss transparent, cone 2–3.

	Blue	Green	Black	Buff	Brown	Orange	Red
White lead	51.50	40.5	51.50	73	73	73	73
Zinc oxide	17.50	17.50	17.50	17.50	17.50	17.50	17.50
Whiting	29.0	29.0	29	29	29	29	29

	Blue	Green	Black	Buff	Brown	Orange	Red
Feldspar	116	116	116	116	116	116	116
Kaolin	58.50	58.50	58.50	58.50	58.50	58.50	58.50
Flint	35	35	35	35	35	35	35
Cobalt Carbonate	9.9	...	...	...	...	...	...
Black oxide cobalt	...	2	...	...	...	...	...
Black oxide copper	...	8	...	...	...	...	...
Best black underglaze	...	...	9	...	...	...	...
Cobalt carbonate	...	...	9.9	...	...	...	...
Brown underglaze 228	...	...	...	5.28	...	...	...
Brown underglaze 228	...	...	...	...	25	...	...
Light brown underglaze	...	...	...	...	...	25	...
Pink oxide	...	...	...	...	...	...	50

Each of the above glazes were ground $1^1/_2$ hours in a ball mill. A tablespoonful of a thin gum arabic solution was added and the batch brushed through a hundred-mesh screen. This glaze remains stationary in the fire and will not run unless greatly overfired or unless applied much too thick.

The best results were obtained with a glaze thickness of $^1/_{32}$ to $^1/_{16}$ of an inch, and fired to cone 2 to 3.

Filling in Design

Upon merging from the biscuit kiln the design outlined in the fired underglaze color was filled in with colored glazes. The thin glaze was applied to the porous biscuit with a medium size sable brush.

It was found better to float the glaze on in two or three thin coats rather than to attempt to build up the proper thickness in one application. In this way thick and thin places in the glaze were reduced to a minimum.

The spaces to be filled in with glaze should not be too large as it is difficult to maintain an even coating over a large area. It was also found best to build up one space at a time to the right thickness ($^1/_{32}$ to $^1/_{16}$), before proceeding to the next. Care should be taken to maintain this thickness right up to the flat outline of underglaze color.

The Background Glaze

After the various parts of the decoration were carefully filled in with glaze to the desired thickness the piece was set upon a whirler and a very thin coat of buff and orange brown glazes were sprayed upon it. The buff was first sprayed over the whole piece and the orange brown was then blended in principally at the top and bottom to obtain a shaded effect. Care was taken to keep this background glaze quite thin, especially over that portion occupied by the pattern, much of which was filled in with glaze.

The Fire

The glazed wares were fired in an oil burning muffle kiln of the usual type, to cone 3, for a period of 12 to 14 hours.

I have hesitated to use the word inlay in the description of this problem for the reason that it is not strictly an inlay process, since the whole background of the piece is applied with the air brush and is superimposed over the filled-in design.

The difficulties were lessened when the underglaze outline was used, as described, to separate and define the various parts of the pattern; but it was found that this flat outline could be used or not as desired. The results obtained in the pieces where no outline was used were perhaps the more pleasing. There was little trouble experienced in keeping the glaze within the space allotted it on a flat or vertical surface, whether with or without an outline if proper care was taken to keep the thickness as indicated and if the glaze was not overfired.

When no underglaze outline was used the edges of the design were not quite as sharply cut and hard looking, they were softer and more elusive, although still clearly defined and with no evidence of spreading into each other or the background glaze.

The background glaze being sprayed over the whole modifies somewhat the colors used in the raised parts of the design but this serves to blend and harmonize the colors with each other and the background, and ties them all up together.

This little problem presents no undue difficulties to the student capable of making and applying glazes. If the directions given are carefully followed the result should be an attractive bit of pottery and a renewed appreciation and respect for those early American potters, the Red Men.

University of North Dakota
Grand Forks, North Dakota

THE USE OF GELATINE IN GLAZE APPLICATION[1]

By Albert C. Gerber

ABSTRACT

Painting with gelatinized glaze offers distinct advantages. A high grade hide gelatine should be used, and careful regulation maintained in all steps of the process. High clay mixtures gelatinize with greater difficulty than those whose contents of ground material are large. Loss from rubbing or chipping of glaze becomes a minimum.

A method of glaze application which despite some rather interesting aspects as well as commendable features, has attracted little attention in the ceramic industry at large, is that of painting the glaze after it has been mixed with a gelatine solution and chilled. In sanitary ware plants employing fire-clay bodies, this method of glazing has been common procedure for many years and is fairly well understood, and in occasional plants manufacturing vitreous sanitary ware either by the one-fire or the two-fire process, it likewise is in use. It is believed, however, that brief discussion may possibly suggest its use in other branches of the industry.

Advantages One conspicuous advantage of the gelatine method of glazing ware is the possibility of applying glaze evenly to a green piece. Dipping a complicated piece of ware obviously is not a procedure capable of easy manipulation or of even glaze distribution. By the method under discussion, the glazing of a green piece of ware no matter how intricate the shape, becomes very simple indeed.

A second notable advantage is the toughness of the glaze coat after it has dried. It has literally been glued to the surface of the piece, and as a consequence, rubbing or chipping off during kiln placing is reduced to a minimum.

Another advantage is the ease of maintaining an even coat of glaze on ware which is of such shape that even dipping is attended with some difficulty. Wherever glaze tends to accumulate because of slight flow, a coat or two can be skipped. Also to be remembered is the facility for evenly superimposing a glaze on an engobe, or of using two different glazes should that be desired.

Quality of Gelatine Before outlining the method, a word on gelatine itself will not be irrelevant. There are five or six general classes of glues and gelatines, and in each class a great number of grades. For this particular purpose a straight hide product seems to be best suited. It cannot be unduly stressed, to provide a strictly high grade product.

The chief requirement of a gelatine for this use is that its jelly strength be great, and hide gelatines are generally considered the strongest and most reliable.

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[1] Presented at Atlantic City Meeting, Feb., 1924 (Whitewares Division).

The form of the gelatine whether flake or ground is quite immaterial. Ground flues (or gelatines) can be used more conveniently, but there appears to be some prejudice against their use due to greater ease of adulteration. Ground glue is to be preferred, if equal in quality to a good flake glue. The higher grade glues when in flake form are usually light in color, and nearly transparent.

The odor of a glue gives some indication of its source or condition. Glue which has a slightly offensive odor is not considered of the highest grade. The nature of the process obviously demands a gelatine of good keeping qualities. This can be determined by allowing a bucket of glaze made up with gelatine to stand in the shop for a number of days, and noting the odor and condition of the gelatine at intervals. Glues with good keeping qualities will stand at least 48 hours in a moderately warm temperature without developing an offensive odor or showing any appearance of decomposition. Some indication of a glue's "keeping" qualities is its reaction to litmus. A slightly acid glue is slightly preferable to one which is neutral or alkaline, for the reason that slight acidity discourages the growth of organisms which promote the decomposition of glue.

By "jelly strength" is meant the firmness or elasticity of the jelly formed by cooling a glue solution of specified strength. Strong glues usually have a high jelly strength. Unfortunately, there is no standard unit for expressing "jelly strength" and consequently there is no way of purchasing it on a "jelly strength" specification which is equally intelligible to all buyers and sellers. Various testing apparatus, based usually on the penetration of some object into a jelly of fixed proportions, are used by different manufacturers, but each laboratory expresses its test results in its own terms and no two agree. Inasmuch as for ceramic purposes the gelatine is never used alone, but always as a medium of suspension, any test which disregards the slip or glaze to be used with the gelatine, is likely to fall short of its purpose.

Contrary to what might naturally be expected, high content of ground material does not necessarily impose the severest test on a gelatine. On the other hand a slip or glaze with a high clay content can generally be relied upon to show first symptoms of weakness in a gelatine. Explanation for this can possibly be found in the acidity of the gelatine, which by promoting coagulation of the clay, accelerates the tendency to settle, and thereby counteracts the influence of the gelatine to uniformly suspend the slip.

Example of Use The following practical test is offered as a means of trying out gelatines for this use. A slip consisting of 60% sand flint, 20% No. 1 Florida clay, and 20% English china clay is prepared by ball milling for a short time. After setting to a weight of 26 oz. per pint, 10 quarts are measured off into a 3-gallon bucket.

Seven ounces of the gelatine under test are carefully dissolved in one quart of hot water, added to the bucket through a sieve to remove small lumps, and carefully and uniformly stirred into the slip. If the slip is cold, it should be warmed somewhat before the gelatine is added. After standing for five or six hours at a temperature of approximately 35°F, the contents of the bucket should be firmly jellied, with no covering of water. The stiffness of the jelly should suffice to sustain the weight of an average one pint Mason fruit jar, the jar and contents weighing at least one pound. Of several glues tested in this manner, the one producing the firmest jelly would under ordinary circumstances be the best.

For comparative tests of jelly strength, the common method of determining the relative firmness of the jellies is with the outstretched fingers. The finger tips are very sensitive to slight differences. It is to be noted that the quantity of gelatine suggested in the test is a minimum, and that products which can only meet its conditions with an additional ounce or two of gelatine can safely be classed as high grade.

Possible Uses

Definite comment on the ceramic use of gelatine becomes all but impossible owing to the endless variety of circumstances surrounding its use. Different glazes or engobes, as the case may be, will require varying amounts of gelatine; weather conditions vary; green and biscuit ware require different treatment.

One may consider three sources of control in this method of glazing—(1) the specific gravity of the slip or glaze, (2) the proportion of gelatine added to it, and (3) the operation of painting the glaze on the piece. With a slip or glaze at a set weight, experimentation will quickly determine the proper amount of gelatine to be used. It should suffice to produce a firm jelly under all conditions of weather. During warm weather, as a rule, it becomes necessary to increase the amount of gelatine used. It will generally be found to be true that engobes, particularly, if moderately high in clay, will require a larger amount of gelatine than the average glaze. Increasing the proportion of gelatine facilitates application but at the same time diminishes the weight of glaze applied on the piece. In this same connection it is to be noted, that mixtures lean in gelatine slide poorly while being painted, and as a consequence exert considerable "pull" on preceding coats thereby inviting trouble through the formation of blisters. Of importance, also, is that no coat of slip or glaze should be applied until the preceding coat has thoroughly dried. During sudden changes of weather this frequently becomes a source of trouble.

Finally, it is noteworthy that although comparatively simple in all its details, the use of gelatine in glaze application does at times invite a somewhat narrow margin for the maintenance of uniformity. The following will illustrate. Continuous complaint from the glazing department over the lack of uniformity of their glaze led to examinations of the glue being used and investigations into the care and accuracy exercised in setting the glaze, without leading to an explanation. Finally it was discovered that one of the glaze agitators was leaking slightly, and that consistently there was trouble when preparing glaze from this agitator—this despite careful regulation of the weight of the glaze after it had been drawn off. This glaze incidentally carried no soluble ingredients which might pass off with the leakage and thus slightly derange its composition. Explanation may lie in the possibility of a small loss of colloidal matter in the water which leaked out. At any rate the disturbance was no longer noticed when this particular tank was abandoned.

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ORIGINAL PAPERS

EFFECT OF URANIUM IN VARIOUS TYPES OF GLAZES[1]

By Oscar E. Mathiasen

The object of this study is to determine what effect different glaze compositions have on uranium as to shade, color uniformity in burning, and behavior under different kiln conditions. One per cent of uranium oxide was used in all cases. This is the most active form of uranium used in glazes for coloring, and will show the best indications of any variations which may occur. Having once established a glaze which under varying kiln conditions shows a normal uniformity of color, it is only reasonable to assume that if an uranium frit or stain is substituted in this same glaze the result will be a glaze even more reliable in its action, as an uranium frit or stain is generally considered more reliable than uranium oxide.

The following are some of the results and conclusions of previous papers dealing with the action of uranium oxide in glazes.

1. F. H. Riddle:[2]

Glazes with high lead content	Orange color
Glazes with low lead or free of lead	Yellow
Glazes with boric acid content	Lemon yellow

2. E. T. Montgomery and I. A. Krusen:[3]

Porcelain glazes containing 10% uranium oxide	
gave under reducing conditions	Jet black colors
gave under oxidizing conditions	Yellow mottled colors

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[1] Presented at the Atlantic City Meeting, Feb., 1924 (Terra Cotta Division).

[2] *Trans. Amer. Ceram. Soc.*, **8**, 210 (1906).

[3] *Ibid.*, **16**, 355 (1914).

3. R. M. Howe:[1]
   Uranium grays and blacks produced under reducing conditions.
4. L. R. Minton:[2]
   This paper concludes with stating that uranium oxide is an uncertain and tricky oxide where soft coal is used.

These references show the many different effects that can be produced with one coloring oxide: Orange, lemon, yellow, black, mottled yellow, and olive green. The outstanding conclusion, however, concerns the different effects of oxidation and reduction on uranium oxide.

Two series of glazes were made, one by eliminating or substituting certain parts of a glaze which is normal except for a somewhat high clay content, and the other series by treating in a like manner a glaze low in clay and high in feldspar content. The formulae and batch weights are shown in Table I.

Materials common to all terra cotta plants were used. The analyses of three feldspars used are given in Table II. The uranium oxide used is the yellow oxide.

It was intended to fire all glazes under both oxidizing and reducing kiln conditions. Four attempts were made but in each an oxidizing atmosphere prevailed. In the opinion of the writer, the color of several of these glazes would have varied under irregular firing, and new trials will be fired to prove this. The different shades produced under normal conditions are as follows:

SERIES 1. GLAZE A AS BASIS

Glaze	Component eliminated	Color under normal kiln conditions with 1% uranium oxide
A	......	Buff cream—Slight green tinge
B	China clay	Clear cream
C	Barium carbonate	Cream—Slight green tinge
D	Zinc oxide	Gray cream
E	Tin oxide	Lemon yellow
F	Whiting	Cream—Did not mature
G	Substituting magnesium carbonate	Buff cream—Slight green tinge
H	Conn. & Godfrey	Lighter buff cream—Slight green tinge

SERIES 2. GLAZE J AS BASIS

Glaze	Component changed	Color under normal kiln conditions
J	......	Clear cream—Lighter than previous shades
K	China clay addition	Cream—Decided green tinge
L	Talc eliminated	Buff cream full glaze
M	Cornwall stone and Maine feldspar used	Buff cream full glaze

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[1] *Trans. Amer. Ceram. Soc.*, **16**, 494 (1914).

[2] *Ibid.*, **9**, 777 (1907).

TABLE I

EFFECT OF URANIUM ON VARIOUS TYPES OF GLAZES

		Feldspars												
		Godfrey	Connecticut	Maine	Cornwallstone	Flint	China Clay	Ball Clay	Whiting	Barium Carbonate	Zinc Oxide	Tin Oxide	Magnesium Carbonate	Uranium Oxide
$0.30\ K_2O$ $0.34\ CaO$ $0.17\ BaO$ $0.17\ ZnO$	*Glaze A* $0.50\ Al_2O_3\ 2.96\ SiO_2$ $0.089\ SnO_2$	...	...	450	100	85	75	50	100	100	40	40	..	10.4
$0.30\ K_2O$ $0.34\ CaO$ $0.17\ BaO$ $0.17\ ZnO$	*Glaze B* $0.40\ Al_2O_3\ 2.75\ SiO_2$ $0.089\ SnO_2$	...	...	450	100	85	..	50	100	100	40	40	..	9.7
$0.36\ K_2O$ $0.41\ CaO$ $0.21\ ZnO$	*Glaze C* $0.61\ Al_2O_3\ 3.60\ SiO_2$ $0.11\ SnO_2$	...	...	450	100	85	75	50	100	...	40	40	..	9.4
$0.36\ K_2O$ $0.92\ CaO$ $0.21\ BaO$	*Glaze D* $0.61\ Al_2O_3\ 3.60\ SiO_2$ $0.11\ SnO_2$	...	...	450	100	85	75	50	100	100	..	40	..	10.0
$0.30\ K_2O$ $0.34\ CaO$ $0.17\ BaO$ $0.17\ ZnO$	*Glaze E* $0.50\ Al_2O_3\ 2.96\ SiO_2$	...	...	450	100	85	75	50	100	100	40	..	..	10.0
$0.46\ K_2O$ $0.27\ BaO$ $0.27\ ZnO$	*Glaze F* $0.77\ Al_2O_3\ 4.54\ SiO_2$ $0.14\ SnO_2$	...	...	450	100	85	75	50	...	100	40	40	..	9.4
$0.28\ K_2O$ $0.26\ CaO$ $0.13\ BaO$ $0.15\ MgO$ $0.16\ ZnO$	*Glaze G* $0.47\ Al_2O_3\ 2.80\ SiO_2$ $0.08\ SnO_2$	...	...	450	100	85	75	50	80	80	40	40	40	10.9
$0.33\ K_2O$ $0.33\ CaO$ $0.17\ BaO$ $0.17\ ZnO$	*Glaze H* $0.49\ Al_2O_3\ 2.77\ SiO_2$ $0.09\ SnO_2$	450	100	...	...	85	75	50	100	100	40	40	..	10.9

Additional firings were made in the cases of glazes A-B and J, to compare their behavior under varying kiln atmospheres.

Glaze A changed from a cream to a lemon yellow while J on the same piece under the same action remained unchanged. The explanation of this difference in behavior probably is the absence of china clay and the greater fusibility and therefore solvent action of J. When china clay was added to glaze J in Series 2 to form glaze K, the shade changed from

TABLE I (*continued*)
EFFECT OF URANIUM ON VARIOUS TYPES OF GLAZES

			Feldspars										
		Godfrey	Connecticut	Maine	Cornwallstone	Flint	China Clay	Ball Clay	Whiting	Talc	Zinc Oxide	Tin Oxide	Uranium Oxide
Glaze J	$0.38\ K_2O$ $0.36\ CaO$ $0.06\ MgO$ $0.16\ ZnO$ $0.36\ Al_2O_3$ $2.88\ SiO_2$ $0.11\ SnO_2$	378	270	...	...	64	..	49	108	43	46	48	10
Glaze K	$0.38\ K_2O$ $0.36\ CaO$ $0.06\ MgO$ $0.16\ ZnO$ $0.57\ Al_2O_3$ $3.13\ SiO_2$ $0.11\ SnO_2$	378	270	...	...	64	98	49	108	43	46	48	11
Glaze L	$0.41\ K_2O$ $0.38\ CaO$ $0.20\ ZnO$ $0.44\ Al_2O_3$ $2.98\ SiO_2$ $0.11\ SnO_2$	378	270	...	...	64	..	49	108	..	46	48	9
	$0.32\ K_2O$ $0.40\ CaO$ $0.07 MgO$ $0.21\ ZnO$ $0.47\ Al_2O_3$ $3.40\ SiO_2$ $0.13\ SnO_2$	...	...	378	270	64	..	49	108	43	46	48	10

TABLE II—ANALYSES OF FELDSPARS

	Connecticut	Godfrey	Maine
SiO_2	72.20	74.49	70.50
Al_2O_3	17.88	14.48	15.37
Na_2O	2.98	5.18	3.04
K_2O	6.25	4.45	9.00
FeO	0.17	0.15	0.07
MgO	..	0.40	0.13
CaO	0.14	0.57	0.29
Loss on ignition	0.34	0.38	0.39
	99.96	100.10	98.79

a clear cream to a cream with a decided green tinge under normal kiln conditions. This comparison demonstrates the possibilities of an uranium oxide glaze which will fire uniformly under varying kiln conditions. With glaze J as a base, a glaze will be developed which will not craze and still retain this characteristic of color uniformity.

Where glazes A and B were treated in a like manner, A showed the same tendency to turn green while B remained practically the same. Having in mind that possibly one reason for the discoloration of glaze A under certain conditions might be the assimilation by barytes or barytes and china clay of soluble salts, carrying perhaps iron impurities from the body, which under reducing conditions might cause this green shade, a clay batch was prepared using sodium carbonate as a soluble salt. On trials of this, glazes A and B were applied and fired. The result was that the sodium carbonate boiled out in spots under the glaze and the color of glaze A over each of these spots is distinctly green. In glaze B the same effect was produced but to a less degree.

The results of this study demonstrate that the coloring power of uranium, in the form of the oxide is governed by the glaze ingredients and by the firing, and shows the possibilities of forming an uranium glaze, preferably in the form of a frit containing uranium, which will burn uniformly in color under varying kiln conditions.

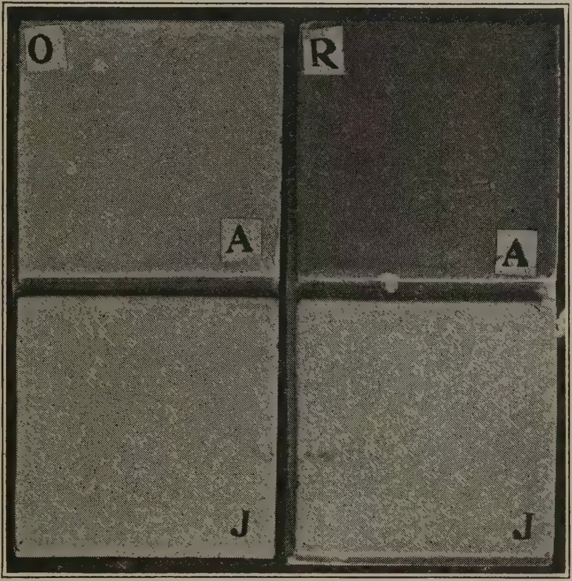

FIG. 1.

Discussion

SECRETARY CLARE: Mr. Mathiasen how did you get reducing conditions and in what sort of kiln?

MR. MATHIASEN: We have no indicator; no way of testing this out. It is only presumed from the color change, that there must have been reducing conditions.

SECRETARY CLARE: This is a very interesting and valuable paper inasmuch as we are all bothered with color variation. It should be of value to the laboratory in explaining some of these so-called variations. A great many time variations are blamed on the kilns that possibly are not due to the kilns.

MR. MINTON: We worked on uranium glazes making these experiments in a small kiln where the conditions could be fairly well controlled. In that kiln we maintained oxidizing conditions and also reducing conditions by "smoking." We also found when we used reducing conditions we never knew what we were going to get.

CERAMIC RAW MATERIALS, DRIERS AND DRYING[1]

By G. F. Metz

ABSTRACT

A description of certain types of rotary driers used for the drying of such ceramic materials as kaolin, chalk, china clay, whiting, fullers' earth, enamel frit, glass sand, feldspar and various chemicals.

While a raw material drier is an apparatus for driving off free moisture from materials, it does so by the application of heat or by air absorption, and is thus distinct from a dehydrator which extracts moisture by mechanical means, and from a calciner which drives off the combined moisture and other volatiles usually by roasting at high temperatures.

The more common problems of drying have to do with the drying of nonmetallic minerals, as for instance, the drying of coal before pulverizing in cement plants, sand and stone for use as a mix with hot asphalt in paving plants; phosphate rock before grinding in fertilizer plants; clays in plants producing for the pottery, paint and rubber industries; fullers' earth in the oil refining industries; gypsum in the plaster manufacturing plants; salts, coke and chemicals in chemical works.

As this paper deals primarily with the drying problems of ceramic materials no attempt will be made to cover any but those types of driers used in this industry. It has been found necessary, in order to handle several materials economically in the various processes used in the ceramic industry that these materials be dry. As they do not always occur bone dry in their natural state and as water is added to some during the process, a machine to remove the excess moisture becomes necessary.

There are two forms or methods of drying by mechanical means, and these are direct heat and indirect heat. These may be classified according to the type of drier used as follows:

Direct heat	Indirect heat
Direct-fired rotary drier	Indirect-rotary drier (steam)
Semi-direct fired rotary drier	Indirect-fired rotary drier (with combustion gases)

No one drying machine has been developed which will satisfactorily eliminate moisture from all materials. It is necessary to use a design suitable to the physical and chemical characteristics of the material. A few examples of those which have been used for some time and the reasons for their use will be described.

Drying of Feldspar and Quartz

Feldspar, one of the most common of the materials used in the ceramic industry, usually occurs in a fairly dry state but in cases where it does not it should be dried in order to pulverize it properly. The writer knows of one specific case where the capacity of grinding mills decreased 20% during a period when the moisture content increased to 6% in the initial feed as compared with the usual moisture of less than 2% during the dry seasons of the year. In the handling of feldspar through a drier, contamination with iron is absolutely prohibitive. A drier of the direct heat type with some minor modifications has been developed for this use.

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[1] Presented at the Atlantic City Meeting, Feb., 1924(Whitewares Division).

Free Public Library, Newark, N.J.

The crushed feldspar is fed through a wooden or tile-lined spout into a revolving drum, the feed end of which is slightly higher than the discharge end. This drum is lined with silex or quartzite blocks set in cement. By the rotation of the drum and its inclination or slope, the material travels slowly from the feed end to the discharge end of the drum where it is dropped out through a stationary discharge end with silex lined discharge spout. A brick furnace is next to the discharge spout, this furnace having the grates some distance away; also baffle walls between the grates and the opening from the back wall of this furnace into the discharge head.

Silica, which also must not be contaminated with iron is now being dried in the same type of drier with fairly good efficiencies, the driers used being exactly the same as those for feldspar except that the lining is a high grade and very hard silica brick, which allows higher temperatures to be used than with the silex lining, thus giving greater capacities and fuel efficiencies for the same size machine. With both the feldspar and the silica driers, coke must be used for fuel.

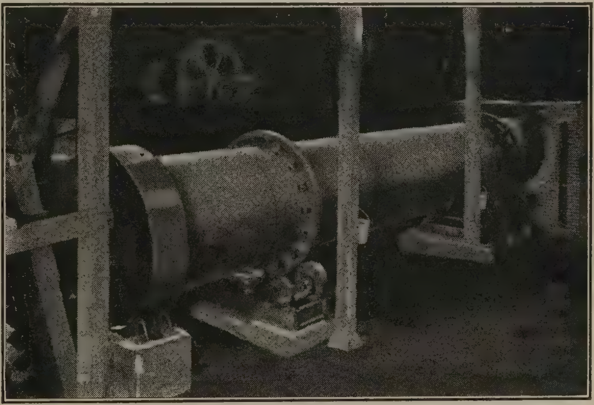

Fig. 1.—Feldspar and quartz drier.

Drying of Frits

A modification of the direct heat form of drying with a resultant increase in thermal efficiency of about 20 to 25% was brought about by Wm. B. Ruggles, some thirty years ago, and has since been elaborated on in the production of the double shell rotary drier. This type of drier is now being used to dry enamel frit in sanitary ware plants as it comes from the water quenching pits. In this type of drier, known as the semi-direct heat or two-pass drier, the heat is first drawn through the inner shell and returned through the showering material in the annular space between the inner and outer shell. By such a method the heat is used at the higher temperatures by radiation and at the lower temperatures by direct contact with the returning gases of combustion. The increase in thermal efficiency, literally meaning less fuel required per unit of product dried, is brought about by this utilization of the gases "going and coming" so to speak. The material is fed at the high or furnace end of shell and discharged at the opposite or low end (Ruggles-Coles Specification). This is probably the most efficient type of drier manufactured from a capacity and fuel standpoint and it is also used on some clays when coke or anthracite coal is used as fuel.

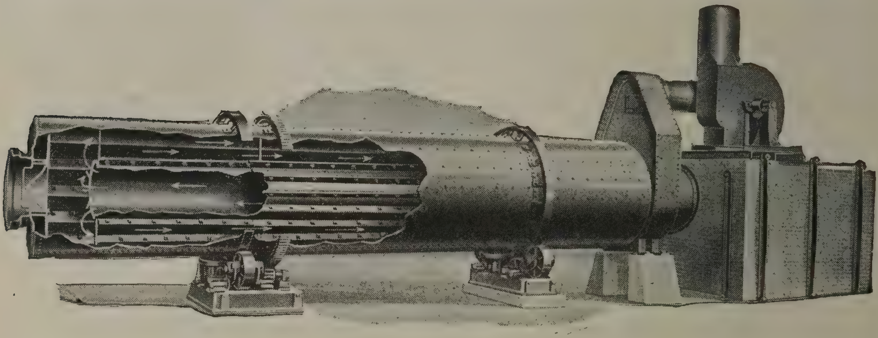

FIG. 2.—Semi-direct heat drier for frits.

Drying of Clay Filter Press Cakes

For drying lump or filter pressed white clays, the only type of drier that has given satisfaction is an indirect heat type wherein the gases of combustion do not at any time come into contact with the material being dried. This type of drier is used in 80% of the kaolin and china clay fields of this country, including the well-known clay fields of South Carolina and Virginia, as well as England, France and Belgium for the dry-

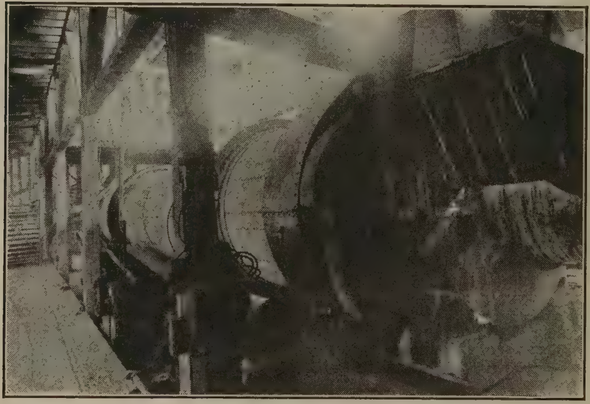

FIG. 3.—Indirect heat drier for chalk clay and filter press cake.

ing of chalk and white clays. It is also used for drying talc in the Vermont talc fields.

This type is also a double shell drier. The gases of combustion are brought down the central cylinder as in the semi-direct heat drier but at the rear end they enter a header and pass back in ducts attached to the inside of the outer shell. The material being dried is fed into the annular space between the cylinder and the ducts, falling, due to rotation of the shell, alternately on the hot inner shell and ducts until it reaches the discharge end which is slightly lower than the feed end, at which point it is discharged through holes in the shell into a head with spout. Two fans or one fan and stack are used, one fan to draw the gases of combustion through the inner shell and the ducts; the other fan or stack to draw the moisture that has been driven off from the material out of the drum. This drier gives off very little dust and what is given off is easily collected due to the small volume of air that is mixed with it.

With all of the above types of drier, some dust is created in the drying process, but very efficient dust collectors have been devised by the manufacturers of some of these machines so that the dust loss is almost negligible.

Drying of Clay Slips or Slurries

For drying clays which are not filter-pressed and those which contain so much water that they will flow as a liquid the so-called atmospheric drum type drier is used.

In the indirect rotary drum drier, the steam is supplied to the interior of the drum, thus heating the whole surface of the drum. The drum, revolving at slow speed in a pan containing the wet material, takes up the material in a thin layer, drying in one rotation. The material is discharged with the aid of a scraper on the downward side of rotation. The action is similar to that of the rotary continuous filter press. This drier must not be mistaken for the commonly known rotary drier, and is used only where the material is in a liquid state and primarily for pasty materials.

Driers in General

There are many other special types of driers used in this industry. Under this head come the traveling conveyor types and the tray types which are used in drying those partially finished or finished articles which cannot be agitated. These, however, are designed and built for the plant in which they are installed and no standard types that would cover a large number of installations have been designed.

An idea of the extent to which rotary driers are used may be obtained from a few facts gathered from the records of one of the largest drier companies:

Of the three types of rotary driers above outlined over 1500 have been installed in this country and abroad, nearly every state in the union having anywhere from one to fifty driers. In addition to the great number of ordinary materials as partially noted above, they are drying wood chips, leacher refuse, pumice stone, iron oxide, etc., within limits that heretofore had been considered too severe for handling by the present method.

Materials are dried not only to facilitate further handling, but to reduce grinding and shipping costs, to prevent possible ruin and increase in repairs to supplementary equipment, to aid in mixing and to allow for a more rapid and less expensive calcining or burning.

Hardinge Company
York, Pa.

CLAY PREPARATION[1]

By T. A. Klinefelter

ABSTRACT

A brief description of clay preparation by washing, which practically eliminates defects due to pop outs and bad stains which are a constant source of annoyance under the usual methods of terra cotta clay preparation.

Terra cotta body mix is prepared in several ways. Sometimes the clays are weighed up just as they come from the cars, and dumped into a wet pan where the batch is tempered with water and mixed a few moments. Or the clays may be reduced to a uniform size before tempering, and tempered and mixed in a pug mill.

So long as the process is in the hands of experienced workmen even the crudest method seems to give fairly good results in point of working qualities, shrinkage, etc. Unfortunately, the batches do not always receive good uniform treatment.

There are several things which the preparation is expected to accomplish, chief of which are working qualities in the plastic state and uniform shrinkage out of the kiln. We trust to luck and the supplier to keep out those impurities which are likely to cause "pop outs," etc.

I believe it will be agreed that there is quite a little loss at times from this careless and indifferent mixing. While the remedy might cost more than the present charges for terra cotta warrant it is worth while to know in what direction betterment may be accomplished.

I am not prepared to say just what does cause all of the various "pop outs." I can say, however, that with the same clays there will be practically no loss from "pop outs," etc., when prepared as are the clay mixes for sanitary ware. The proportions and identically the same clays are used in the making of bath tubs and wash trays as are used for terra cotta but with much less loss from imperfections.

Moreover, the clay itself seems to be more plastic and have better uniform working qualities than the usual terra cotta batch. This latter being the case, it rather naturally follows that the shrinkage should tend to hold more uniform.

The Suggested Process

The process consists in blunging or washing the clay content of the batch, screening the slip over 80-mesh lawn and then filter pressing. From the filter press the clay goes to a wet pan where the grog is mixed with it. The wet pans are lighter weight than is usual where the batch is mixed raw, so the grog tends to stay better to size. After the wet pan treatment the mix is aged and then pugged.

---

[1] Presented at the Atlantic City Meeting, Feb., 1924 (Terra Cotta Division).

The blunging insures an even mixing of clay utterly impossible by any other process. This gives it uniformity of plasticity or working qualities, and as a corollary, other things being equal, uniform shrinkage.

The screen culls out the pebbles of quartz and pyrites and other minerals which would cause trouble by pop outs and dark spots. These pebbles under a wet pan would be crushed and distributed.

With the clays thoroughly blended and cleansed from pebbles the wet pan is given every advantage to work the grog thoroughly into the clay and to develop the maximum plasticity.

An Experience

While the filter-presses were shut down for a considerable period of time the wad clay had to be made in the wet pan without previously being blunged together and lawned. We found that instead of the wads hanging together in lengths of two feet and over, they were very short and broke off in pieces 4″ to 6″ long and even less. Although various mixes, and longer periods of grinding, etc., were tried it was impossible to get nearly as good results as when the clay was first washed.

Clean Grog

A good deal of trouble is due to the grog. Part of the grog is made from broken ware, and sometimes this ware contains pieces of brass fittings which get through and cause the old familiar friend, "Mr. Green Spot."

In crushing and grinding of grog a good deal of very fine dust is produced which is not used. Some of this, along with some scrap, is mixed with new clay in a wet pan, run through a brick machine into brick shapes. The bricks are burned and crushed to make grog. These grog bricks fill out where most firms would buy old saggers.

By using our own ware and uncontaminated new clay, trouble from impurities is reduced to a minimum. Of course, since the clay is not washed and screened there is some chance of impurities being introduced by these grog bricks.

Kiln furniture is much superior when made from washed clays. It is doubtful, however, if the cost warrants carrying it that far.

The process here recommended is costly and perhaps most terra cotta jobs do not warrant this expense. It would pay, however, in the case of certain types of lower story or interior work, such as glazed ornamental work.

BELVIDERE, ILLINOIS

A CERAMIC DECORATIVE PROCESS SUITABLE FOR PUBLIC SCHOOL USE[1]

By Paul E. Cox

Introduction

This is the process used by the Pennsylvania Dutch potters in making the wares shown in the collections of the Pennsylvania Museum. The result is effective because of the strong contrasts, and the technique is one easily mastered. The technique lends itself to the execution of the simple designs possible to secure from classes of average talents in design work.

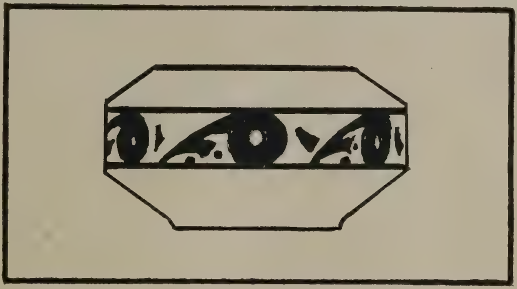

Fig. 1.

The Clay

Any red burning clay that can be used for brick and tile making will serve. The wise teacher will select a clay that has the most pleasing red, and which will be rather plastic. The clay should be washed, screened through a sixty-mesh sieve and dried to the proper stiffness in plaster of Paris molds, unless a clay washing outfit is part of the school equipment.

Forming the Wares

The pieces may be formed in any way desired by the teacher. The only necessary precaution is to keep the ware in such a way that no pieces will become more dry than what is known as leather hard.

Recipes

A suitable white slip is made up by stirring the ingredients in a stoneware jar with water the following ingredients:

25 pounds Kentucky ball clay
25 pounds Georgia kaolin
15 pounds of flint
5 pounds of whiting
30 pounds of feldspar

Screen through the sixty-mesh sieve, let settle and decant the water until the slip is thick enough for use.

A suitable glaze has the following ingredients:

145 pounds of white lead
44 pounds of whiting
52 pounds Georgia kaolin
72 pounds of flint

The glaze is to be prepared in the same way as the slip is prepared.

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[1] Recd. May 15, 1924.

Applying the Slip

The leather hard piece of pottery is plunged into the slip until the slip covers all of the outside of the piece even with the rim. The slip must be thick enough so that the coating on the pottery will completely mask the red clay. This must be worked out by the individual but 24 ounces to the pint is usually about right, for the density of the slip.

After slipping the piece of ware, the piece must be set down and left to dry. When the piece is leather hard again the slip is removed from the places where it is not desired, as for example, the bottom or rim.

Decorating the Piece

The decoration is executed by cutting away the white slip coat so that the design is brought out by the red clay of the body underneath. When the design work is completed the piece is allowed to dry completely and should then be biscuited to about cone 010. It is better to do all carving on the slip coating while the piece is leather hard as chipping in undesired places is more easily avoided.

Glazing the Piece

The biscuited piece is simply plunged into the jar of glaze, care being taken that an even coating is obtained and that the coat is not too heavy nor, on the other hand, too light. The ware should then be fired to cone 01.

An Example

The piece shown in the illustration was executed by the author from a clay not exploited but found at Eldora, Iowa. The piece was thrown and turned, dipped as described into the slip, then set on the wheel again and the surplus slip from the bottom and rim turned off. The design was then developed by cutting away the white slip. The result is a creamy white bowl, brownish red inside, on the rim, and in the designed portions, as the piece came from the glost kiln. This piece was fired in the ordinary oil fired studio kiln common to schools.

Suggested Variations

Colored glazes can be used instead of the colorless glaze. The slip can be stained by the use of prepared stains. Underglaze colors can be used on the slip coating, yielding lively color effects, similar to water colors. The body might be made up from white burning materials and the slip stained, or the body might be stained also.

Sources of Raw Materials

Raw materials can all be had from the various advertisers in the *Journal of the American Ceramic Society.*

Department of Ceramic Engineering
Iowa State College
Ames, Iowa

DISTRIBUTION OF KAOLIN AND BAUXITE OF THE COASTAL PLAIN OF GEORGIA[1]

By R. T. Stull[2]

ABSTRACT

The commercial deposits of sedimentary kaolins and bauxites occur in the Lower Cretaceous of the Coastal Plain. The kaolins vary from "hard clay" to flint clay on one hand to "soft clay" on the other. The hardness of the clays apparently depends on the free silicic acid content. They are difficult to slake and filter-press. The soft clays are washed for the filler and ceramic trades. Evidently the clays were originally hard clays, the soft clays originating from the hard clays by leaching out of the free silicic acid. The bauxites were evidently derived from soft kaolin through decomposition and removal of the silica. The bauxites occur as lenses embedded in larger lenses of kaolin. These bauxites were probably derived from soft clay by laterization. A proposed classification of the sedimentary kaolins and bauxites is given.

The Georgia Coastal Plain, an area of approximately 35,000 square miles, lies to the south of the Piedmont Plateau. The contact between the two divisions known as the "Fall Line" represents an irregular line across the state from Augusta through Milledgeville and Macon to Columbus.[3]

A strip along its northern border 220 miles long and from 40 to 50 miles wide is known as the "Fall Line Hills." This strip lies between the Fall Line to the North and the Dougherty Plain to the South and comprises an area of approximately 9,500 square miles. It is within the area of the Fall Line Hills that the sedimentary kaolins and bauxites of commercial importance are found.

Origin of the Sedimentary Kaolins

Evidences indicate that the Piedmont Plateau was a comparatively level area for a long period of time during which vast beds of primary kaolin were formed through decomposition of the crystalline rocks. Prior to Cretaceous time the Piedmont Plateau experienced an upheaval with a tilting to the southeast producing a rearrangement of drainage with the general course of the streams to the southeast.

The products of decomposition consisting of kaolin, quartz sand, feldspar grains and mica, with other minerals in lesser amounts, were carried by the streams to the Coastal Plain. During their progress a sorting action occurred in which the coarser materials were dropped as the velocity of the streams lessened.

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[1] Recd. May 15, 1924.

[2] Assistant General Industrial Agent, Central of Georgia Railway Company.

[3] The writer is indebted to the following publications for many valuable references:
Geo. E. Ladd, "Clays of Georgia," *Bull.* **6,** Ga. G. S.
Otto Veatch, "Clay Deposits of Georgia," *Bull.* **18,** Ga. G. S.
Otto Veatch and Lloyd William Stephenson, "Geology of the Coastal Plain of Georgia," *Bull.* **26,** Ga. G. S.
H. K. Shearer, "Bauxite and Fullers' Earth of the Coastal Plain of Georgia," *Bull.* **31,** Ga. G. S.

The finest clay particles remaining in suspension were carried out and deposited in lagoons and quiet bodies of fresh water off shore where flat topped lenses of secondary kaolin were formed over long periods of continuous sedimentation.

These clay lenses vary in extent from small areas a few inches in thickness up to deposits 40 feet and more in thickness and covering areas of more than a square mile. Records of artesian wells bored in Wilkinson County show these lens-like strata, alternating with white, yellow and brown sands, extending to great depths; in one case more than 500 feet. That these kaolins were fresh water deposits is indicated by the fact that in so far as known they contain no marine fossils, lime, gypsum or manganese nodules.

The important white sedimentary clays of Georgia belong to the Potomac or Tuscaloosa group of the Lower Cretaceous, and were evidently laid down contemporaneously with the fire clays of New Jersey, both showing the same relative position to the Fall Line.

Although the two clays are similar geologically, ceramically they are distinctly different in their physical properties. The Georgia sedimentary kaolins are comparatively white, low to lacking in fluxes, contain considerably less iron oxide, burn to a white to cream color, and are decidedly more refractory. The differences in their physical properties are due mainly to the differences in the composition of the parent rocks from which they originated.

With the exception of a few rare cases, the Eocene and Tertiary deposits of Georgia are thinner, smaller in extent and inferior in quality to the Cretaceous clays. The Lower Cretaceous sediments (Tuscaloosa Group) rest unconformably upon the ancient metamorphic and crystalline rocks corresponding to those of the Piedmont Plateau. In the Fall Line Hills between the Chattahoochee and Ocmulgee Rivers the Upper Cretaceous lies unconformably upon the Lower Cretaceous. To the east, between the Ocmulgee and Savannah Rivers, the Upper Cretaceous is lacking.

The Eocene strata or later formations rest unconformably upon the Upper Cretaceous and where the latter is absent the former lies unconformably upon the Lower Cretaceous. The Lower Cretaceous is exposed where the upper strata are lacking or have been removed by erosion so that the Lower Cretaceous outcrop occurs near the Fall Line and extends in a belt entirely across the state. This belt varies from 2 to 30 miles in width.

Bordering this strip is an area from 5 to 20 miles wide covered with overburden 4 to 40 feet in thickness above the kaolins and bauxites, while the peaks of the hills sometimes rise to a height of 80 feet above the clays.

The Lower Cretaceous outcrop together with the adjoining area covered with thin overburden, form an area 20 to 30 miles wide extending across the state in a southwesterly direction from Augusta to Columbus. It is within this area that the beds of kaolin and bauxite occur near the surface where mining can be carried on at a very low cost.

The region has experienced minor organic disturbances such as lifting, tilting and warping. These movements have not been of sufficient magnitude to disturb the clays appreciably after their deposition. They are massive and apparently lacking in laminated structure, indicating continuous deposition of material of the same nature.

No faulting or folding is observed and slickensides are rare. Where the surface has not been disturbed by erosion, the top of the clay lens lies on the same plane, dipping to the southeast about 6 to 10 feet per mile, while the average dip of the Coastal Plain surface is 3 to 5 feet per mile.

Formation of Bauxite

Evidences indicate that the bauxites of the Coastal Plain were derived from the alteration of secondary kaolin. The process of alteration has been one of removal of silica, alkalis and alkaline earths with the resultant concentration of alumina, ferric oxide and titania. Frequently deposits will show gradations of material from kaolin on one hand to bauxite on the other.

Of the different theories advanced for the formation of bauxite, that of laterization[1] appears to be the most rational, though it does not offer a satisfactory explanation to account for the origin of some of the Coastal Plain bauxites.

The bauxites occur as lenses imbedded in larger lenses of kaolin. Frequently bauxite lenses are found completely enveloped in very fine-grained, compact kaolin, which is generally massive and almost impervious to water. Those bauxite lenses found in the top of the clay show indications of erosive displacement of the original top covering of kaolin.

The kaolins are so "tight" grained and compact that the percolation of water appears difficult if not impossible. The kaolin lenses, therefore, lack the loose or porous structure for free penetration of water essential to the progress of laterization.

The Tuscaloosa Group of the Lower Cretaceous in which the kaolins occur is practically devoid of plant remains so that vegetable growth or vegetable decay apparently was not an important factor in the alteration of the kaolins.

The kaolins are so resistant to water penetration that they contain scarcely enough moisture when freshly mined to mold into shape readily by dry-pressing. Rain water which finds its way through the overburden readily is unable to penetrate the kaolin appreciably and issues along the slopes as numerous springs and marshy patches. Frequently the top of a kaolin deposit can be traced up to a mile or more by following the line of springs where no outcrops show.

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[1] See C. O. Swanson, "The Origin, Distribution and Composition of Laterite," *Jour. Amer. Ceram. Soc.*, **6** [12], 1248–60 (1923).

Spring water issuing from the top of the kaolin invariably shows a "milkiness" or opalescence even in the dryest season. When allowed to stand in a glass-stoppered bottle for months it fails to become clear or to form a sediment. An "opalescent" spring is a good indication of a deposit of kaolin.

That such waters contain a much higher silica content to alumina than the kaolinite ratio is indicated by chemical analyses. In the following table is given the silica and alumina content of spring waters[1] occurring in some kaolin and bauxite districts of the Coastal Plain, although it is not known definitely that these waters come in contact with the kaolins. The silica-alumina ratios as calculated from these analyses are given in the last horizontal column.

Sample	A	B	C	D	E	F	G
SiO_2, Grains per U. S. Gallon	0.513	0.321	0.583	0.280	1.224	0.828	2.385
Al_2O_3, Grains per U. S. Gallon	0.047	0.058	0.140	0.012	0.047	0.023	0.292
Molecular SiO_2-Al_2O_3 Ratio	18.55	9.40	7.10	39.65	44.26	61.19	13.88

Sample A.	Macon County—12 miles north of Oglethorpe.
Sample B.	Houston County—8 miles southeast of Fort Valley.
Sample C.	Twiggs County—Near Dry Branch
Sample D.	Bibb County—6 miles east of Macon.
Sample E.	Wilkinson County—1 mile west of Toomsboro.
Sample F.	Washington County—8$^1/_2$ miles west of Sandersville.
Sample G.	Glascock County—Deep well water supply of Gibson.

As compared with the silica-alumina ratio of "2" for kaolinite, it is evident that the silica is much more soluble than the alumina and is being removed at a greater rate. However, the silica removed by spring water at ordinary temperatures is evidently free silicic acid for the most part rather than the combined silica of the clay.

Proposed Classification

The Georgia sedimentary clays from different localities vary considerably in their physical properties. In hardness, they vary from that of flint clay through to the very soft and friable variety. Their color in the natural state is from a cream, light gray and light blue to white. In the burned condition the colors range from light buff to white, depending upon the content of ferric oxide and titania. For convenience they may be classified as follows:

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[1] The silica and alumina contents as given in the table were taken from the complete analyses of waters as given by Dr. S. W. McCallie in "Mineral Springs of Georgia," *Bull.* **20,** Ga. G. S.

(1) Flint Clays
(2) Hard Clays
(3) Semi-hard Clays
(4) Soft Clays

Inasmuch as the predominating evidence indicates that the bauxites were derived from the soft clays, the above classification may be extended to include:

(5) Bauxite Clays
(6) Bauxites

(1) The flint clays are represented by those found in Glascock County near Gibson. Though they cannot be classed strictly as flint fire clays there is a similarity in many of their physical properties. Like flint fire clays they are hard, break with a conchoidal fracture, do not slake, are short or lacking in plasticity, but develop a weak plasticity when water-ground to a very fine condition. Their color is usually cream to light gray or drab. The silica content is comparatively high as indicated by the silica-alumina ratio which varies from 2.4 to 2.8. They show practically no fire shrinkage below cone 12 and deform at cones 31 to 33. The flint clays of Georgia are comparatively scarce having been found in only a few localities. Flint clay is mined at one point and shipped to Birmingham, Alabama, where it is used in the manufacture of refractories.

(2) The hard clays are light cream to white. They are very fine-grained, comparatively free from grit, break with a conchoidal fracture, crumble down to angular fragments, $^1/_8$ to $^1/_4$ inch in diameter, when placed in water but do not slake to a slip condition on standing. These fragments, however, soften in water so that they can be crushed between the thumb and finger. When kneaded or tempered with water (as for example in a wet pan) they are exceedingly plastic and moldable. When placed in slip condition by long continued agitation or grinding, they settle with difficulty and the supernatant water remains strongly opalescent indefinitely with an appearance suggestive of the presence of silicic acid.

On filter pressing, the water comes through milky at first but soon clogs the filter sacks making it impossible to obtain firm cakes. Objects molded from the thoroughly tempered clay dry safely though slowly and show a very high dry strength. Their deformation temperatures are from cones 33 to 34. The hard clays evidently would be valuable for a considerable part of the bond clays in saggers and crucibles requiring high temperatures. They are more widely distributed than the flint clays and are found frequently in Washington, Wilkinson and northeastern Twiggs Counties.

(3) The semi-hard clays are most abundant of the different varieties. They are cream to white in color and burn light buff to white. They slake

to a grain form about the size of flax seed and blunge to a good slip on long continued agitation. They settle slowly on standing, leaving a light opalescence in the supernatant water. Under comparatively high pressure, they filter press slowly forming a comparatively soft cake, though one that can be handled. They are very fine-grained and plastic and show good bonding strength. Their deformation temperatures vary from cones 33 to 35. When used in combination with grog, sand or other non-plastic material, with even as low as 35 per cent raw clay content, they mold readily and dry and burn safely.

The semi-hard clays are known to exist in lenses, some of which are more than 650 acres in extent, and vary in depth from 10 to over 40 feet. A large lens near Gordon has a known maximum depth of 52 feet. Due to their great abundance, ease of working and refractory properties, they offer unparalleled opportunities for the manufacture of refractories.

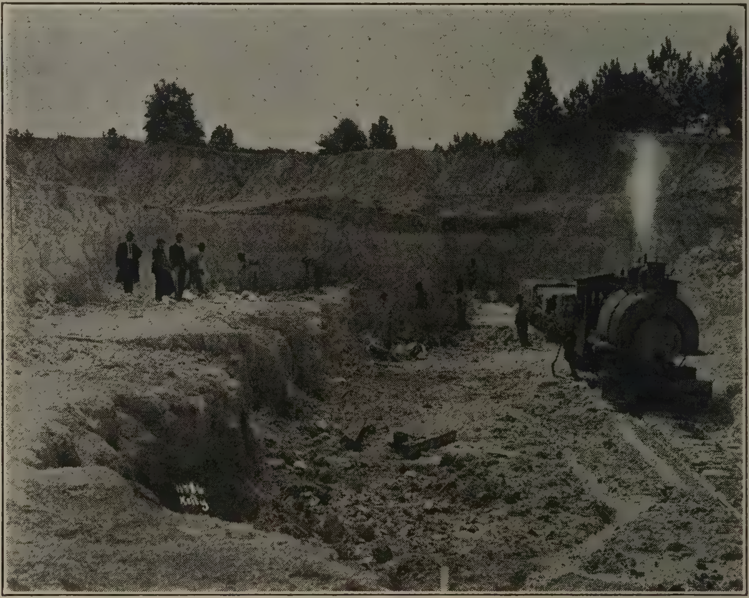

FIG. 1.—Kaolin mine showing bauxite lense in the top.

(4) The soft clays are cream and light blue to white in the natural state and burn cream to white. They slake and blunge readily to a slip condition and filter press without difficulty. The soft clays are mined and washed extensively for the filler and ceramic trades. They are friable, very plastic and show low bonding strength. They deform at cones 33 to 35. When used in quantities of more than 30 per cent in plastic bodies, they are susceptible to cracking in drying, but work satisfactorily in dry

press bodies such as compositions for floor and wall tile and electrical insulators.

(5) The bauxitic clays are those with a silica-alumina ratio of 1.8 to 0.8. They are apparently mixtures of clay and bauxite. As the silica-alumina ratio decreases, the ease of slaking, plasticity and dry strength also decrease. Usually a soft "oolitic" structure is visible from traces of pin head size up to those of about $^3/_4$ inch in diameter. These clays vary in color and hardness from snow white and very soft to the gray buff rock known locally as "chimney rock." This rock is sufficiently soft so that it can be quarried and cut readily but hardens on exposure. Its name is derived from the fact that it has been used locally for the construction of chimneys from the time of the earliest settlers. The deformation temperatures of the bauxitic clays are cones 35 to 38. They are found abundantly over large areas associated with kaolins and bauxites. Their distribution, ease of mining and refractory properties make the bauxitic clays ideal materials for the manufacture of high grade refractories.

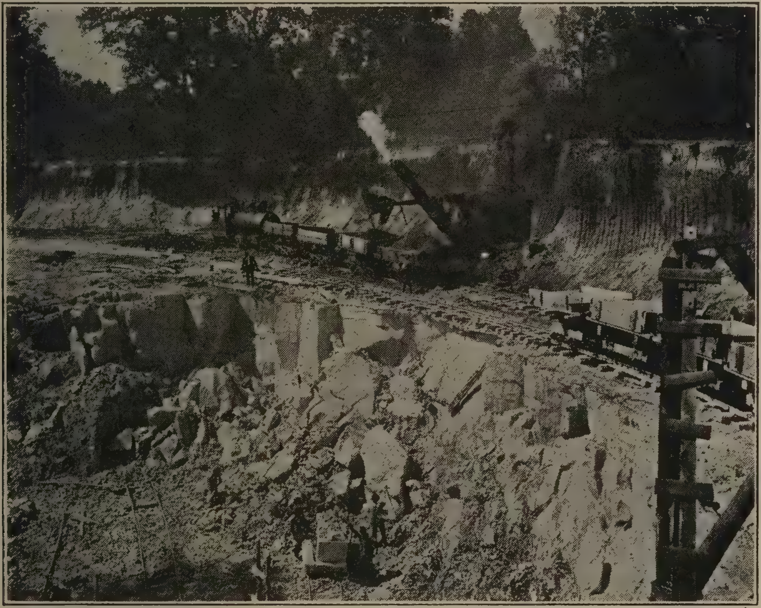

FIG. 2.—Mine of soft kaolin near McIntyre, Ga.

(6) The bauxites show an alumina content of from 52 to 61 per cent. Their deformation temperatures vary from cones 37 to 40. Those containing 52 to 56 per cent alumina are classed as "low grade" and those containing over 56 per cent as "high grade."

Inasmuch as there is no sharp dividing line between bauxitic clays and bauxites, as one frequently grades into the other, some "chimney rock" would fall within the low grade bauxite class. Chimney rock, therefore, appears to lie on the border line between bauxitic clays and bauxites.

Generally, the high grade bauxites occur as the bottom portion of the lens with low grade bauxite above and bauxitic clay or kaolin below. Frequently, chimney rock is found above and in contact with the low grade bauxite. The contact between the chimney rock and the low grade bauxite and that between the low and high grade bauxites is, in general, sharply defined. Both the high and low grade bauxites are valuable raw materials for the manufacture of high grade refractories. The high grade bauxites are used in the manufacture of alum, aluminum, and abrasives to a limited extent.

The difference between the flint and hard clays is very marked and apparently no well-defined gradation exists between the two. The most noticeable differences are those of plasticity and hardness. The flint clays when crushed and moistened with water are short and friable while the hard clays are very plastic and strong.

On the other hand, clays are found representing all stages between the hard and soft clays. The examination of a large number of chemical analyses from different sources shows that the hard clays are a little higher in silica than the soft clays, and that there is a decrease in silica as the clays become softer. Empirically, the hard clays are near 1 Al_2O_3, 2.25 SiO_2 which grades down to and around 1 Al_2O_3, 2.0 SiO_2 for the soft clays.

That the hardness of these clays is due to the presence of free silicic acid is evident. Its presence would explain why spring waters flowing from the top of the clays are always opalescent and show a high analytical content of silica. The presence of silicic acid in the hard and semi-hard clays would also account for their difficulty to slake and filter press and for their high degree of plasticity and bonding strength. The lack of free silicic acid in the soft clays would also account for their ease of slaking and filter pressing, the clearness of the water coming from the filter press and also their lower bonding strength.

Whether silicic acid was present at the time the clay beds were formed or whether it was formed or introduced years after deposition is problematical. Evidence tends to show that the clays originally were hard clays and that the soft clays resulted through removal of free silicic acid. The flint clays apparently are secondary derivations from the hard clays due to their higher content of free silicic acid which underwent a hardening action by conversion of silicic acid to "set gels."

The edges of the clay deposits are usually soft along the slope of the hills where the clay has been beveled down by erosion and later covered with a thin sandy overburden. However, in mining back into the hill, where the clay and overburden have not been disturbed, the clay generally grades into the semi-hard and hard varieties.

In the large massive lenses which have been well protected by a heavy overburden of clay-like fullers' earth, the hard and semi-hard clays sometimes extend from top to bottom of the lens. In other cases the top 10 to 15 feet is hard or semi-hard clay and the bottom 10 to 20 feet soft clay. The division between the two is quite abrupt and easily recognized when prospecting by boring.

The two different strata may have been laid down at different times with a sufficient time interval for the alteration of the lower clay from the hard to the soft variety before deposition of the top clay, or the entire lens originally may have been soft clay and the top hard portion formed by infiltration of silicic acid (which is very doubtful) from the "gummy" impure fuller's earth which usually overlies the hard clays. Where the "gummy" overburden is lacking or has been replaced by sand, the underlying clay is usually the soft variety.

Deposits are found in which the entire lens is soft clay. In stripping the overburden during mining, these clays usually show pot holes and irregular surfaces indicative of disturbances by erosion and long periods of exposure to atmospheric conditions. Later these clays were covered with sand often containing white clay pellets, some as large as a bushel basket, which were torn up from the clay beds by swift running waters and deposited with the sandy overburden. Under such conditions there would be opportunity for alteration from the hard to the soft variety, and under favorable conditions alteration even to bauxite. Although isolated cases occur where hard and soft clay and bauxitic materials are found in close proximity, the bauxites, in general, are found associated with the soft clays. The hard clays are generally absent.

No systematic field work has been done to cover the clay areas of the Georgia Coastal Plain since the report of Otto Veatch in 1909, published in *Bulletin* 18 by the State Geological Survey. Considerable development has since taken place and numerous undeveloped properties have been located.

In 1909 only one clay mine was reported in Wilkinson County and at that time it was inactive. Twiggs County during that year produced approximately 85 per cent of the kaolin of Georgia amounting to nearly 25,000 tons. During the past year, Wilkinson County produced over 65 per cent of the output of Georgia amounting to more than 85,000 tons.

Twenty-four counties lying wholly or partly in the Coastal Plain are known to contain secondary kaolins or refractory clays of the "kaolinitic" variety.

These counties are:

Baldwin
Bibb
Columbia
Crawford
Glascock
Hancock
Houston
Jefferson
Jones
Macon
Marion
McDuffie
Quitman
Randolph
Richmond
Schley
Stewart
Sumpter
Talbot
Taylor
Twiggs
Warren
Washington
Wilkinson

Space will not permit of listing and describing all known kaolin, refractory clay and bauxite properties of the Georgia Coastal Plain offering commercial possibilities. To show the development to date, a list of the producing mines is given below:

Albion Kaolin Company,	Hephzibah, Richmond Co.
Harbison-Walker Refractories Co.,	Gibson, Glascock Co.
Akron Pigment Company,	McIntyre, Wilkinson Co.
Aluminum Flake Co. of Georgia,	McIntyre, Wilkinson Co.
Edgar Brother Company,	Edgars, Wilkinson Co.
Edgar Brothers Company,	Dedrich, Wilkinson Co.
Edgar Brothers Company,	Toddville, Wilkinson Co.
Republic Mining Company,	Wriley, Wilkinson Co.
Moore and Munger,	Claymont, Wilkinson Co.
Savannah Kaolin Co.,	Gordon, Wilkinson Co.
Gordon Kaolin Company,	Gordon, Wilkinson Co.
Stevens, Incorporated,	Nadine, Wilkinson Co.
Stevens, Incorporated,	Stevens Pottery, Baldwin Co.
American Clay Company,	Dry Branch, Twiggs Co.
Georgia Kaolin Company,	Dry Branch, Twiggs Co.
John Sant and Sons Company,	Dry Branch, Twiggs Co.
Golding Sons Company,	Butler, Taylor Co.

At the present time, in Wilkinson County, eight active mines are producing kaolin, one is producing refractory clay and one is mining high grade bauxite. In the "Directory of Commercial Minerals in Georgia and Alabama along the Central of Georgia Railway," issued by the Industrial Department, seventy-seven undeveloped properties and operating mines are listed in Wilkinson County alone, and since that publication was issued, twenty-one properties of commercial possibilities have been added.

INDUSTRIAL DEPARTMENT
CENTRAL OF GEORGIA RAILWAY
SAVANNAH, GA.

PLANER ECONOMIES[1]

By H. R. Straight

History

The planer, for the primary winning of clays and shales was first used in Germany, over thirty years ago, for the excavation of peat, and the removal of glacial overburden for strip mining.

The first use of the planer principle in this country may be attributed to J. M. Powell, of the Indiana Drain Tile Company, of Brooklyn, Indiana, in 1909. This machine ran back and forth, on a straight face, and was operated in somewhat the same manner as the German machine. It was found that there were very few places where such a machine could be used on account of two open ends being required to the face, and a shale or clay being necessary that would stand up almost vertically in the face. This type of machine was made for a few years by the Arbuckle Company, and was installed in several different plants. There is at least one of these machines yet working at Lexington, Ohio.

On account of the high face and greatly differing strata worked at the plant in which the writer is interested, the planer idea was carefully investigated in 1912. It was at once seen that it was not possible to use the old principle, on account of the pit being below the level of the surrounding country, and on account of bad faults in the face. A different type of machine was, after a year of experimenting, then developed and largely perfected. It is clearly remembered how the first summer of operation showed up seventeen distinct troubles. The machine was then shut down and rebuilt, and each and every trouble was entirely eliminated.

Recently a modification of this machine has been made and placed on the market, which makes use of the Adel method of swinging in a circular path, but does not have the advantage of some of the basic principles which will be outlined briefly later on. It is not the intention of the writer to criticize in any way the principles that they have used, but rather to bring out correct mechanical principles, as they have been found after nine years of experimenting and development.

Advantages

The advantages of cutting into a face of shale, clay, or soft rock, so that the surface cut will be circular, are almost obvious, on account of the self-supporting face.

It is also clear that a machine that cuts a face which slopes back away from vertical has great advantages where there are faulty bank conditions.

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[1] Presented by P. E. Cox at the Atlantic City Meeting, Feb., 1924 (Heavy Clay Products Division).

Those who have operated steam shovels know how a fall from the face of a deep clay bank has sometimes almost covered up the machine.

The greatest advantage of the planer, is the taking of a small cut and mixing of the fine particles of the entire deposit from the bottom to the top of the face. This eliminates seven distinct difficulties ordinarily found in a ceramic heavy ware industry.

1. No large chunks can come from a shale planer. Practically one-fourth could go directly into the pug mill. None need be crushed with a primary crusher.
2. There is no clay or shale down to become soaked up during wet weather.
3. Practically no frozen material to grind in the winter, and that part which is frozen is small in percentage and size of chunks.
4. There is no loose material down to become dried out and thus cause coarseness in the pugged clay and the consequence, hard molding.
5. There is no unmixed difficult drying strata, to cause heavy drier loss.
6. There is no unmixed easily fused and refractory strata to cause high kiln loss.
7. There are no units turned out of the plant that will cause a heavy shipping or rattler loss, because of accidently being made wholly of a clay from a strata from which only ware of weak structure can be produced.

Besides eliminating the troubles just stated the planer offers the following five distinct advantages.

1. The power consumption of the machine is so low that the cost of the explosive ordinarily used in a shale bank will pay for the power.
2. The clay preparation is so nearly complete as delivered from the planer that the saving of power in the crushing plant will be almost equal to the power the planer consumes.
3. Because of the small amount of material exposed to weather in the face being worked, the initial moisture is kept in and better pugging qualities and better plasticity are secured. This results in a saving of power in the molding and pugging machines to almost the extent of the power required by the planer.
4. Continuous operation of the cutting chain at a constant depth of cut, and the comparatively long time interval of reversing in swinging back and forth requires little attention and practically no skill on the part of the operator. Any man of ordinary intelligence can learn to run a planer in two weeks.
5. A high face with widely differing strata may be worked with no difficulty and often a greatly improved ware is to be had because of different qualities of the strata being mixed.

How the Face of the Bank Should be Worked

The first principle to be recognized is that the machine must be built to dig its own floor, take the cut required, and give the capacity required. It is always safe engineering to design a machine to give the capacity well over that actually required.

Figure A-1 shows the relation of the successive cuts to each other. It is noticed that the distances shown as "X" are distances that the machine travels at the beginning and at the end of each successive cut; from the no cut to full cut, and vice versa. In order to show this, the depth of cut, which is generally around one inch, has been greatly exaggerated and the distance X is also correspondingly exaggerated.

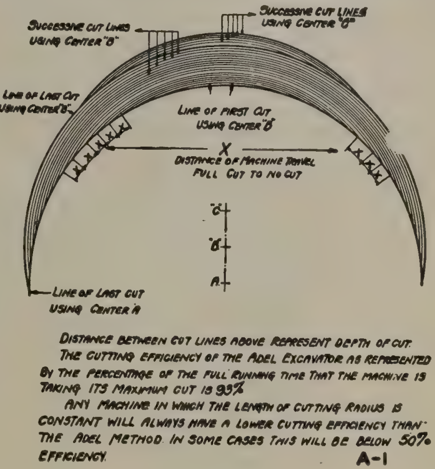

SUCCESSIVE CUT LINES USING CENTER "B"
SUCCESSIVE CUT LINES USING CENTER "C"
LINE OF LAST CUT USING CENTER "B"
LINE OF FIRST CUT USING CENTER "B"
X
DISTANCE OF MACHINE TRAVEL FULL CUT TO NO CUT
C
B
A
LINE OF LAST CUT USING CENTER A
DISTANCE BETWEEN CUT LINES ABOVE REPRESENT DEPTH OF CUT.
THE CUTTING EFFICIENCY OF THE ADEL EXCAVATOR AS REPRESENTED BY THE PERCENTAGE OF THE FULL RUNNING TIME THAT THE MACHINE IS TAKING ITS MAXIMUM CUT IS 93%
ANY MACHINE IN WHICH THE LENGTH OF CUTTING RADIUS IS CONSTANT WILL ALWAYS HAVE A LOWER CUTTING EFFICIENCY THAN THE ADEL METHOD. IN SOME CASES THIS WILL BE BELOW 50% EFFICIENCY.
A-1

Fig. A-1.

The speed of swing is in general six to nine feet per minute, and the distance X on 1″ depth of cut is less than 1 foot on the average. In fact, the time consumed from the end of the full cut until the machine is advanced and brought back again to full cut, is considerably less than one-half minute. This gives a cutting efficiency of around 93%.

In order to secure this quick complete clearing and return to full cut, a fixed radius center and an increasing radius length is used. Special attention is drawn to the first cut with radius center B and also the last cut with same center as shown in Fig. A-1.

Any machine which makes use of a fixed radius length, and which constantly advances the radius center with each new cut must of necessity have a low cutting efficiency per full running time, for the machine must be built to take the maximum cut without breakage. The maximum cut in such a method of operation is only directly ahead of the center. Any swing to either side will cause a constantly thinner cut down to nothing as it swings on each side of straight ahead. In such a case, each cut would be crescent in shape, thickest straight ahead of the center, and always tapering out to a point each way.

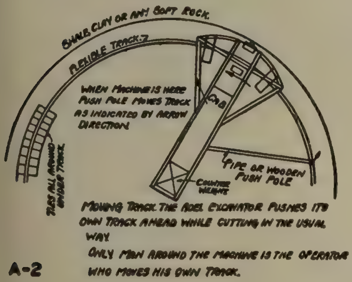

SHALE, CLAY OR ANY SOFT ROCK.
FLEXIBLE TRACK.
WHEN MACHINE IS HERE PUSH POLE MOVES TRACK AS INDICATED BY ARROW DIRECTION.
CAB
TIES ALL AROUND UNDER TRACK
PIPE OR WOODEN PUSH POLE
COUNTER WEIGHT
MOVING TRACK. THE ADEL EXCAVATOR PUSHES ITS OWN TRACK AHEAD WHILE CUTTING IN THE USUAL WAY.
ONLY MAN AROUND THE MACHINE IS THE OPERATOR WHO MOVES HIS OWN TRACK.
A-2

Fig. A-2.

Moving of the Track

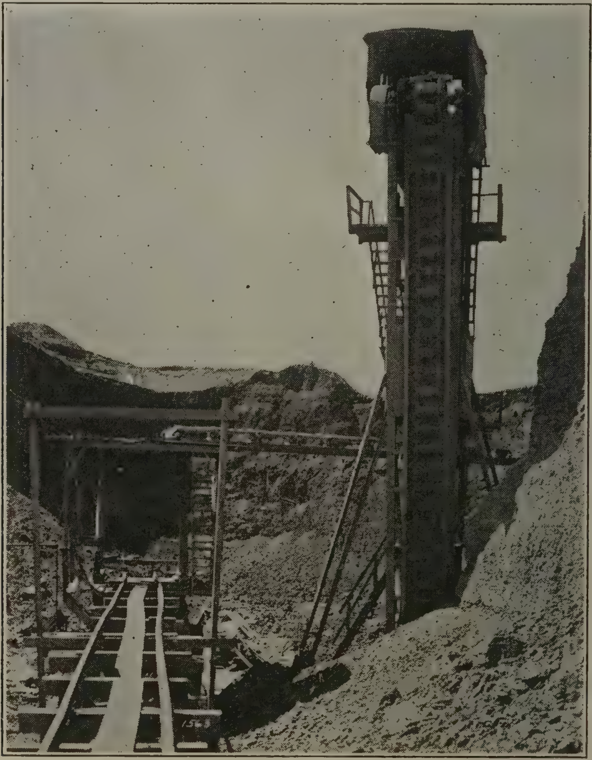
The next consideration is how to move forward the track on which it swings as each successive cut is taken.

Figure A-2 shows how a push pole is used to push the flexible track into any desired advancing position while the machine is operating. The machine need not be stopped for more than the time required to loosen the pole after the track has been advanced to the correct position.

The rollers which support the machine and carry it back and forth around the radius center are comparatively long, and need be at no fixed distance from the center so long as they are on the track.

Which Direction to Cut

After deciding on the way to position the machine in relation to the surface being cut we must now decide whether to cut up or down.



The Adel machine turned beyond its cut showing cutting knives and buckets.

Figure A-3 shows the relative distance through which the shale must break out ahead of the point. This has been found true in ordinary and fairly hard shales. The breaking out angle, in relation to the horizontal stratum line, has been found by observation to average around 45°. Since this angle would be the same whether cutting upward or downward, and since most all shales or soft rocks show practical horizontal stratification, distance A must be shorter than B. A slope of 1 to 5, is in most cases required to make it safe to work faulty faces. Since the breaking out distance from the point is practically in proportion to the power required by the machine it is easily understood why so much more power is required to cut downward than upward.

Another advantage of cutting upward is that under wet conditions the clay will not stick when carried upward with no pressure on it except its own weight as it would if pushed up an incline, as it always must be if cut downward and allowed to fall to the bottom. Even when the clay is not sticky much more power is required to drag it up than to elevate it.

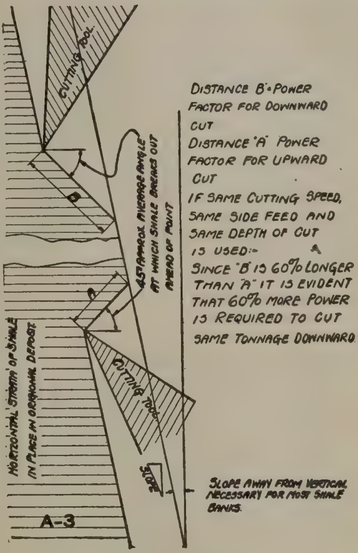

CUTTING TOOL
DISTANCE B = POWER FACTOR FOR DOWNWARD CUT
DISTANCE "A" POWER FACTOR FOR UPWARD CUT
IF SAME CUTTING SPEED, SAME SIDE FEED AND SAME DEPTH OF CUT IS USED:-
SINCE "B" IS 60% LONGER THAN "A" IT IS EVIDENT THAT 60% MORE POWER IS REQUIRED TO CUT SAME TONNAGE DOWNWARD
B
A
45° APPROX. AVERAGE ANGLE AT WHICH SHALE BREAKS OUT AHEAD OF POINT
HORIZONTAL 'STRATA' OF SHALE IN PLACE IN ORIGINAL DEPOSIT
CUTTING TOOL
SLOPE
SLOPE AWAY FROM VERTICAL NECESSARY FOR MOST SHALE BANKS.
A-3

FIG. A-3.

Relation of Bucket Elevator to Cutting Knives

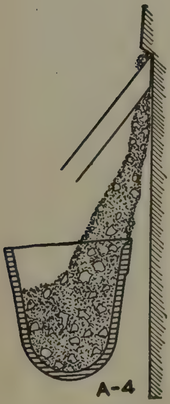


FIG. A-4.

Figure A-4 shows the relation of the elevator buckets to the cutting knives. Several buckets are used to carry the cuttings from one knife. As one bucket is filled, the next bucket below catches what runs over from the one above.

Elimination of Working Troubles

The side banks left behind the machine were so positioned that large falls of weathered shale caused great inconvenience by covering the track leading to the plant. Figure A-5 shows the width of cut *a* resulting from the machine as first designed. By the addition of a conveyor, width *b* of cut is now secured. It is seen by the angle of final repose after the face has weathered down from a 50-foot face the nearest that any of the weathered materials can come to the track is about 30 feet.

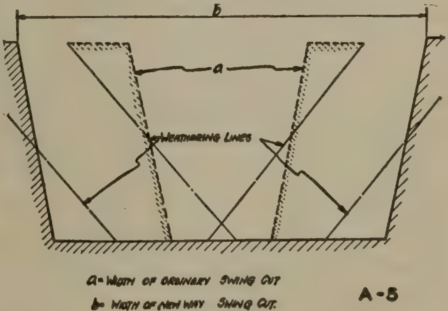
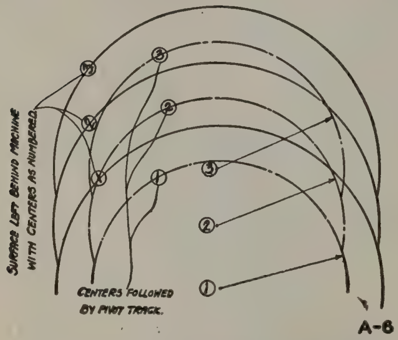

b
a
WEATHERING LINES
a = WIDTH OF ORDINARY SWING CUT
b = WIDTH OF NEW WAY SWING CUT.
A-5

FIG. A-5.

Where the machine is digging itself into a different level, the advantage of being able to swing the machine out at the end of the telescopic conveyor is very readily seen. While the machine is digging itself downward at only a very slight angle as it cuts across and returns from one side to the other this slight angle yields for each swing a net distance of several feet downward. With each successive swing, as shown in Fig. A-6, it is possible to accomplish more than a 12% grade.

By using the loading hopper as a center, and swinging around as shown in Fig. A-7 the width of the cut with our particular machine is over 130 feet. Each successive 30-foot movement of the loading hopper yields over 7000 tons of clay in a 50-foot face. This saves time in moving, in building short sections of track, and in splicing out trolley wires or conveyors. This method leaves a less amount of working surface subject to freezing or drying out, and behind the machine is left a surface circular in shape, and self-bracing.


SURFACE LEFT BEHIND MACHINE WITH CENTERS AS NUMBERED
③
②
①
CENTERS FOLLOWED BY PIVOT TRACK.
A-6

MACHINE CAN DIG ITSELF DOWNWARD AT ANGLE OF 12% GRADE. ON LINE OF PIVOT TRACK CENTERS. THEREFORE EACH ALTERNATION FROM SIDE TO SIDE WILL LOWER FLOOR APPROX 4'0"

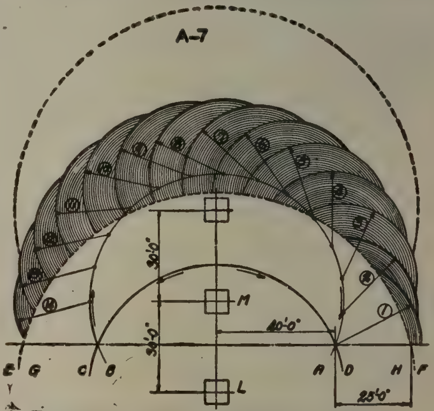
Fig. A-6.

Saving of Labor

One man with such a machine can easily cut and deliver 50 tons per hour. A great many times we have found the operator sitting on the step watching the machine run and yet the machine was running up to capacity.

The Repairs

The starting and stopping of clay machinery contributes greatly to its breaking or wearing out. It is recognized that in such a machine, taking a continual comparatively light cut, the breakage is very small. We cut over 200,000 tons with the first main cutting chain. The knives in gritty shale require resharpening every other day. In chalk rock it is necessary to sharpen the knives only once every two weeks.



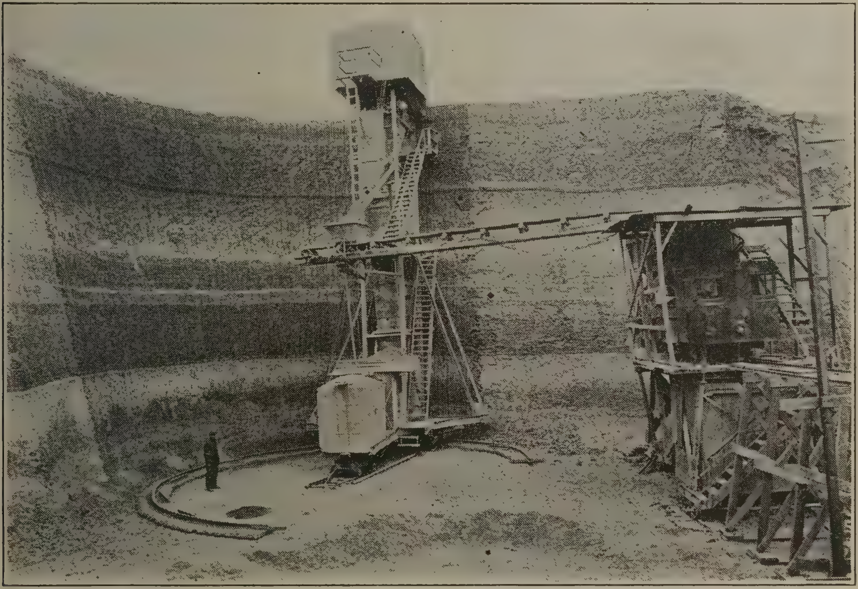
THIS DRAWING ILLUSTRATES NEW METHOD OF USING SHALE PLANER WHICH GREATLY INCREASES ITS CAPACITY.

Fig. A-7.

The Cost

The original cost of a machine that will cut a 50-foot face and deliver a uniform mixture is several thousand dollars less than that of a shovel for the same height of clay bank. The power consumption per amount of material produced is very much less than that for a shovel. The savings over the cost of operating a shovel are almost obvious.

It can be stated from nine years of experience with the original machine at the plant of the Adel Clay Product Co. at Adel, Iowa that the savings made possible by a planer will easily pay for the first equipment costs in less than two years. I would be glad to help any clay worker solve his pit problems if I can.



The Adel, Iowa pit showing a part of the 130′ width of cut.

Discussion

Mr. Smith: Is the idea that clay directly off the face of the bank is in a better condition to work from a weathering standpoint than a clay that has been exposed to the weathering action? I always supposed that weathering action constituted exposure to air and water and that there would be some disadvantage if it were taken directly out of a bank.

Prof. Cox: I am not able to agree with the author that the prevention of weathering is always a good thing. Were it possible to weather the shales in an economical way and gather them as economically as a shale planer will gather them, it would be better to weather them thoroughly. It is not possible however to do so. Since a partial weathering can only be had, and this partial weathering simply causes falling of shale into the pit and in the way of the work of winning the material, the planer effects economies as indicated by the author. They are able to handle their pits more readily than a steam shovel can do the work and so in Iowa they are all changing over from steam shovels to planers.

Mr. Owens: If some of the plants that are using the old type of steam shovel and loading from the pits were to adopt planers they might find some of their scum troubles would disappear.

Mr. Potts: If we permitted weathering we got an increase of scum. It took very elaborate weathering to do any good. A little bit was highly injurious. Thorough weathering might have been of some help but nobody could afford to give it. Mr. Straight's experience as stated is exactly in accordance with general experience.

Mr. Tefft: Mr. Straight claims to have no trouble caused by freezing clay. How does he accomplish this? We are not able to do it.

Prof. Cox: From New Year's until February 1 there was zero steadily. The water that runs over the face will probably only penetrate a little distance into the face of the bank so the frozen part is only a thin crust. When that is cut off, that which is exposed is pretty dry. It is then broken so finely it does not make any trouble.

Mr. Owens: Mr. Tefft's remarks are based on the actual experience with the shale planer which we are running at our plant. You can see what frost in the clay will do, as we can show you that cold weather has an effect on the planer.

Mr. Tefft: We will show you a shale planer that cannot cut through the clay because it is frozen too hard.

Prof. Cox: It must be on account of the way the water runs into the shale. Our shales are not very wet as they lie.

Mr. Straight:[1] We have no difficulty in cutting frozen clay, with our type of machine. We cannot even notice any difference in the cutting, or the power required, until it gets down to about 5° below zero. Lower than this, there seems to be more power required, and the ammeter on the motor shows about 15% more power required when it is 20° below zero. This causes no trouble in the manufacturing process when using boiling hot water for tempering. We have made some of our best runs on days when it was 30° below zero.

We find that a planer lends itself very nicely to finer grinding, for much of the material is already finely cut from the machine. Fine grinding practically takes the place of weathering, and allows us entirely to get away from scumming, which we were formerly bothered with when we used shovels, and wheel-barrows and blasted our face down. This seems to confirm Mr. Pott's opinion.

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[1] Recd. May 3, 1924.

I have just returned from Demopolis, Ala., and Dallas, Tex., where two machines of this type are being used for cutting a hard chalk rock for making Portland cement. This fact would seem to answer the question in the minds of some of the members as to whether or not the planer will cut under difficult conditions. These cement plants absolutely require from 500 to 600 tons per day.

THE OXIDATION OF CERAMIC WARES DURING FIRING.[1]
IV.—THE ABSORPTION OF SULPHUR GASES BY FERRIC OXIDE IN CLAY

By Frederick G. Jackson[2]

ABSTRACT

The nature and amount of absorption of sulphur gases by an almost pure clay to which seven per cent of ferric oxide had been added is studied at various temperatures. Ferrous salts and sulphites were found as traces or not at all. The amount of ferric sulphate increased with increasing temperature on a smooth curve to a maximum at about 450°C, then decreased sharply to almost nothing at 630°C. At its maximum, nearly half of the iron present was in this form. Most of the remaining iron was in an insoluble form called "ferrous sulpho-silicate." On the basis of this work, recommendations are made in regard to kiln fuels.

Introduction

In the preceding paper of this series[3] the conditions leading to the formation of calcium sulphate scum were studied. Although this is the commonest form of scum, there are other sources. Seger[4] speaks of the salts of iron, chromium, and vanadium as possible scum-forming elements. Samples have been brought to the attention of this Station of a buff-burning face brick made from a No. 2 fire clay which had formed a reddish brown scum. This scum proved on analysis to be ferric oxide.

Evidence has also been found in the study of the gases evolved by industrial kilns that there are temperature ranges at which sulphur gases are absorbed in large amounts by iron-bearing clays, without the formation of scum.

It was decided to study this absorption along the same lines as those followed in the previous investigations. (See the second paper of this series.)[5] This study involved a building up rather than a breaking down of iron-sulphur compounds. The general plan of procedure was to make up a clay bar with about 7% ferric oxide, an amount of iron frequently occurring in a red burning clay, hold it at a definite temperature while passing over it a definite amount of sulphur dioxide and trioxide mixed with air and steam in a proportion approaching kiln conditions, collect and determine the sulphur gases not absorbed, and analyze the clay bar for the purpose of finding the amount absorbed. An added feature was the determination of ferrous iron in the bar after absorption. By repeating this process exactly, varying only the temperature at which the clay bar under study was held, the change in the nature and amount of absorbed gases with change of temperature was studied.

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[1] Published by permission of the Director, U. S. Bureau of Mines.

[2] Associate Chemist, Columbus Station, U. S. Bureau of Mines.

[3] *Jour. Amer. Ceram. Soc.*, **7** [6], 427 (1924).

[4] *Collected Writings*, **1**, p. 382.

[5] *Jour. Amer. Ceram. Soc.*, **7** [4], 223; *ibid.*, **7** [5], 382 (1924).

Procedure To simulate the sort of conditions which would attend the firing of a 7% ferric oxide clay in gases containing sulphurous oxide, a train of two electric combustion furnaces, bulbs and sampling bottles was set up. In a combustion tube in the first electric furnace was placed a briquette composed of 60 grams of plastic kaolin and 5 grams of ferric sulphate. In the second furnace was the test briquette composed of 15 grams plastic kaolin and 1 gram of ferric oxide. A Gooch crucible with asbestos mat and potash bulb was connected with the second furnace. Suction was applied to the system by draining a 5-gallon bottle of water.

The heating of the first furnace was so regulated that 1000°C was attained in exactly 75 minutes. At the end of this time and at this temperature the electric current was shut off, but the suction was allowed to continue for 45 minutes more. The heating of the ferric sulphate briquette under these conditions produced an evolution of sulphur gases, water vapor and air, which passed through the second furnace and thoroughly bathed the ferric oxide briquette. This gave opportunity for the formation of a scum.

The first furnace containing the ferric sulphate briquette could be likened to the kiln fire box in which sulphurous coal is being fired. The second furnace containing the ferric oxide briquette corresponds to a kiln set with a red burning brick which is sensitive to scumming by sulphurous gases. The suction produced is equivalent to the draft in the kiln.

The determinations were made on ferric oxide bars heated at various temperatures ranging from 20°C to 680°C. The second furnace containing the test briquette was brought to the desired temperature before any gases were generated or suction applied. This temperature was held constant at the desired temperature throughout the period of exposure to gases from the first furnace.

The suction (the draft) was such as would be caused by two and a half gallons of water being drawn off during the 75 minutes in which the first furnace was being heated up to 1000°C. It was continued at the same rate during the 45 minutes in which the first furnace was cooling.

Method of Analysis The method of absorption and analysis of SO_3 and SO_2 from a gas stream have already been described.[1]

The analysis of the ferric oxide bearing clay bar presented some new features besides the procedure already described. The method was as follows:

When the bar was removed from the combustion tube, it was put directly into a liter distilling flask with 500 cc. of distilled water. The air in the flask was continuously displaced with CO_2 passed through the side branch of the flask. This atmosphere of CO_2 prevented any oxidation of ferrous iron to ferric. A reflux condenser was attached and the contents of the flask boiled for half an hour. The reflux condenser prevented any loss by volatilization. Fig. 1 is a photograph of the entire apparatus, showing from left to right the CO_2 generator, extraction flask and condenser, suction bottle, potentiometer, absorption devices, furnaces, and guard bulb. The gas stream passes from right to left in the picture.

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[1] *Jour. Amer. Ceram. Soc.*, **7** [4], 223 (1924).

This boiling of the ferric oxide-bearing clay bar served to extract into solution all water soluble iron-sulphur salts in the state in which they existed at the end of the treatment. Such salts are freely soluble in water so that repeated extraction, as practiced with calcium sulphate in the preceding paper, was unnecessary.[1] The flask was allowed to cool undisturbed, so that the clay settled to the bottom.[2]

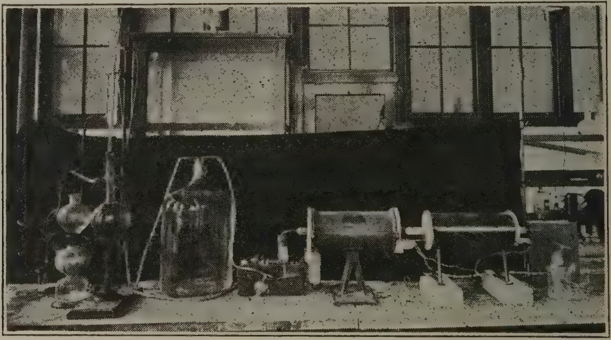

FIG. 1.

To analyze this solution, 50-cc. lots were pipetted into beakers. To one lot, HCl was added in excess, the beaker boiled for five minutes, $BaCl_2$ solution added, and SO_3 determined. To a second lot bromine water and HCl were added in excess, the excess of bromine boiled away, and SO_3 and SO_2 were precipitated as $BaSO_4$ with $BaCl_2$ and determined together.[3] A third 50-cc. lot was added to a beaker containing dilute sulphuric acid and 10 cc. of standard potassium permanganate solution. One cc. of this solution would oxidize about 0.0002 gm. of ferrous iron. It was frequently compared with a standard sodium oxalate solution of exactly this strength and the proper correction calculated and applied. Ten cc. of this sodium oxalate solution was next added to the beaker and then permanganate solution added again until a faint pink color persisted for several minutes. The amount of ferrous iron could be calculated from the amount of permanganate solution used. This delicate determination was repeated several times in each case as a check. Then the remaining liquid in the distilling flask was filtered into a graduated cylinder to determine the exact volume from which the parts were taken. It was then possible to calculate the following data:

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[1] This was tested in one case by a second extraction in which nothing was found.

[2] Clay bars that had been heated to 435° or less slaked in the extraction process. Those that had been heated to 470° or more maintained their shape though sometimes splitting in halves lengthwise. It is interesting to notice that this sintering temperature is about the same as that at which water of constitution begins to be given off.

[3] See second paper of this series for the details of this method, *loc. cit.*

TABLE I

Temp. of Fe_2O_3 bar, °C	Water soluble sulphur unabsorbed by bar as		Water soluble sulphur absorbed by bar as		Total sulphur found	Iron reduced in bar	Sulphur not found
	SO_3	SO_2	SO_3	SO_2			
20	0.0282	0.5945	0.0892	0.0025	0.7144	0.0180	0.1644
240	0.0986	0.5320	0.0652	0.0160	0.7118	0.0	0.1670
295	0.1536	0.4632	0.0824	0.01	0.6992	0.0050	0.1796
350	0.0965	0.5555	0.0924	0.0070	0.7514	0.0110	0.1274
415	0.1172	0.4312	0.1784	0.0[1]	0.7268	0.0080	0.1520
470	0.1177	0.4400	0.1808	0.0[1]	0.7385	0.0090	0.1403
530	0.1615	0.5530	0.0572	0.0040	0.7757	0.0070	0.1031
580	0.2632	0.4608	0.0180	0.0[1]	0.7420	0.0050	0.1368
630	0.2649	0.5135	0.0072	0.0[1]	0.7856	0.0	0.0932
680	0.2654	0.5340	0.0020	0.0[1]	0.8014	0.0	0.0674
No bar	0.2450	0.6338	....	....	0.8788	....	....

Temp., °C.	Weight $BaSO_4$ from SO_3	Weight $BaSO_4$ from SO_3+SO_2
295	0.0600	0.0593
415	0.1300	0.1303
470	0.1318	0.1274
580	0.0132	0.0130
630	0.0053	0.0052
680	0.0014	0.0011

Discussion of Results

This work gives us a different angle on a subject that was left unfinished in the second paper of this series. In the results presented in that paper it was seen that sulphur was not completely evolved by heating iron-sulphur compounds incorporated in clay to 775°C. It was found that the residual sulphur was not dissolved from the clay by water or by dilute aqua regia, even with prolonged boiling. The residual sulphur was found only by splitting up the silicate radical with hydrofluoric acid. It was therefore suggested that ferrous sulpho-silicate was formed.

A survey of the column headed "Sulphur not found" in Table I shows that sulphur has disappeared in this series of experiments as well. In the experiment marked "no bar" the furnace containing the ferric oxide was eliminated. The absorption apparatus was connected directly to the generator furnace, and the entire evolution of SO_3, SO_2 steam and air from it was absorbed directly. The difference between this amount and the amount of sulphur found in each of the other cases is the amount of sulphur that has been fixed as an insoluble compound. This difference in each case is given in the last column of Table I.

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[1] These zeroes are not the result of finding a less amount of $BaSO_4$ from $SO_3 + SO_2$ than from SO_3 alone, but are check analyses in each case, as is shown:

The ferric oxide used was tested and showed an ignition loss of 15.93 per cent. This, in all probability, accounted for practically all of the impurities, leaving 0.8407 gm. of Fe_2O_3 actually put into each bar, or 0.5885 gm. of Fe. How was this iron distributed at the end of each experiment? Whatever iron was reduced must have been in the form of $FeSO_4$. In the experiments made at 20°, and probably at 240°, the SO_2 found may have been in the form of H_2SO_3 liquid in the clay capillaries or it may have been as $Fe_2(SO_3)_3$, ferric sulphite. While this compound is not well recognized, we may, for simplicity, consider that small amounts of it are formed. The bulk of the sulphur absorbed, appearing at first glance, is $Fe_2(SO_4)_3$, ferric sulphate. The insoluble sulphur amounts, however, to more in each case. Let us assume that it has formed some complex like $(FeSO_4)_x(SiO_2)_yZ$ (in which Z may be some multiple of Al_2O_3, or may be nothing) but in which at least the Fe and the S are equi-molecular. From the weight of sulphur, we can then calculate the weight of iron.

TABLE II—DISTRIBUTION OF IRON AT THE END OF EACH EXPERIMENT

Temp. of bar, °C	Fe as $FeSO_4$[1]	Fe as $Fe_2(SO_3)_3$	Fe as $Fe_2(SO_4)_3$[1]	Fe as $(FeSO_4)x$ $(SiO_2)yZ$	Total Fe in S compds.	Fe unattacked as Fe_2O_3
20	0.0180	0.0029	0.0921	0.2876	0.4006	0.1879
240	0.0	0.0187	0.0761	0.2921	0.3869	0.2016
295	0.0050	0	0.0928	0.3144	0.4122	0.1763
350	0.0110	0.0082	0.1005	0.2229	0.3426	0.2459
415	0.0080	0	0.2029	0.2660	0.4769	0.1116
470	0.0090	0	0.2050	0.2458	0.4598	0.1287
530	0.0070	0.0047	0.0621	0.1805	0.2543	0.3342
580	0.0050	0	0.0176	0.2395	0.2621	0.3264
630	0	0	0.0084	0.1630	0.1714	0.4171
680	0	0	0.0023	0.1179	0.1202	0.4683

These results are also shown graphically in Figure 2. The lowest line subtends the amount of iron present as $FeSO_4$. The line next above it and sometimes coinciding shows the occasional traces of $Fe_2(SO_3)_3$ found. Above that is shown the amount of $Fe_2(SO_4)_3$ formed. This increases steadily from 240° to a maximum between 415° and 470°, then decreases again steadily to almost zero at 680°. The amount of ferrous sulpho-silicate formed, while always large, shows first an increase to 295°, then a decrease at 350°. At 415°, the greatest amount is found. The amount of sulpho-silicate then decreases again with increasing temperature steadily except for a slight increase at 580° but there is still a considerable amount formed at 680°.

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[1] In calculating these columns, the weight of S corresponding to the weight of Fe'' found is calculated. This weight of S is then subtracted from the weight of S found absorbed as SO_3. From this difference is calculated the weight of Fe as $Fe_2(SO_4)_3$.

Application to Industry

It is evident from these results that the iron oxide impurity in clay is eager to absorb sulphur from any source while it is being heated until a temperature of about 680°C (1256°F) is reached. There is always iron oxide in the clays used in heavy clay products. There is also sulphur in most of the fuels, wood and natural gas being the only exceptions. Therefore, when a kiln is heated with a sulphur-bearing fuel and the products of combustion come in contact with the ware, the ware will absorb sulphur from the fuel gases. There is always sulphur present in the crude clay, but the amount is appreciably increased in this way. The sulphur in the clay must be burned out slowly at low temperature to insure a sound product. The more sulphur there is, the more delay there

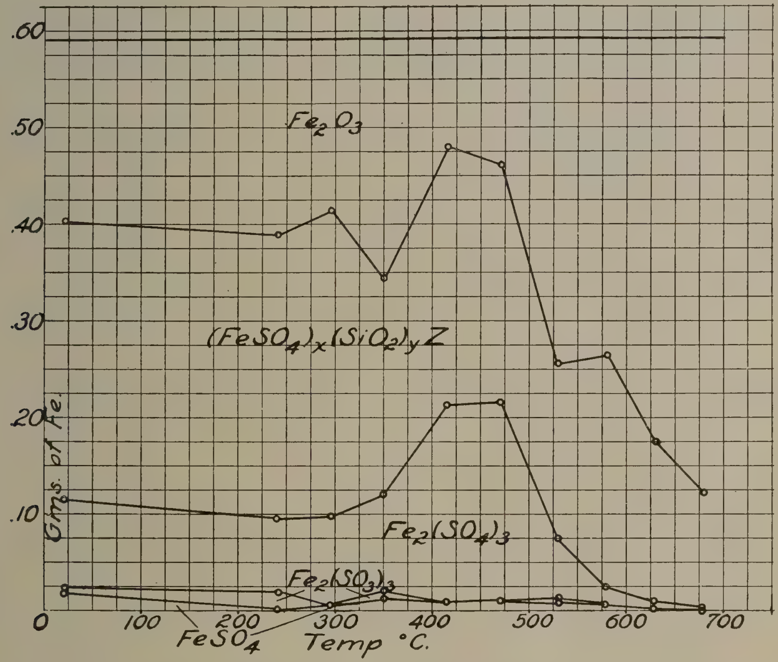

FIG. 2.—Showing the variation in distribution of iron among different compounds with change of temperature.

will be. Delay in burning a kiln means burning more fuel, paying for more labor hours, and getting less output from the equipment. All of these increase cost of production.

In some special cases costs would probably be reduced by firing the first part of the burn with wood, if it is obtainable, even at a higher price per heating unit. When coal is the only fuel available, as is the case on many yards, another course is open. Coal shipments often vary widely in their sulphur content. If it is possible to divide the coal received according to sulphur content, the low sulphur coal should be used to start the burn, the high sulphur to finish it. This is in opposition to the practice at some plants. The natural tendency is to use any old coal to start and save the best to get the higher temperatures. Coal should always be bought on analysis and the sulphur content of each car should be known before the car is set at the plant.

In the next paper of this series, the same problem will be taken up by a study of actual kiln conditions.

CLAY SEWER PIPE MANUFACTURE. V.—THE INFLUENCE OF VARYING LIME CONTENT IN CLAYS UPON SOME PROPERTIES OF SALT GLAZES PRODUCED AT DIFFERENT TEMPERATURES[1]

By H. G. Schurecht[2]

ABSTRACT

Purpose.—The effects of CaO content in clay between 0.15 and 8.22% and the salt glazing temperatures between cone 02 and 10 on some properties of salt glazes were studied.

Brightness.—As low as 1% CaO will prevent clays from taking a bright glaze at low temperatures. Clays containing CaO can best be glazed at high temperatures, above cone 5, providing the Fe_2O_3 content is low. The type of glaze a clay containing CaO will take may be approximately predicted by calculating G in the following equation in which x_1, x_2, x_3 and x_4 represent the percentages of Al_2O_3, SiO_2, Fe_2O_3 and CaO in the calcined clay and T represents the salt glazing temperature in °C.

$$-1.00x_1 + 0.376x_2 - [1.885 + 0.385(1.01253)^{(T-1110)}]x_3 - [1.91 + 2.117(1330-T)^{0.219}]\ x_4 = 100G$$

When G is greater than 0, bright glazes were produced, when between -0.1337 and 0, semi matt glazes were obtained and when below -0.1337 matt glazes were produced.

Color.—Clays high in both CaO and SiO_2 produced greenish yellow glazes at cone 7 on clays containing 5.32% Fe_2O_3 as is represented by the following equation:

$$-1.00\ x_1 + 0.053\ x_2 + 2.68\ x_4 = 100\ A$$

When A is greater than 0, the greenish yellow glazes were obtained.

Thickness.—Raising the salt glazing temperatures and lime content increased the thickness of the glassy and fused portion on the surface of the clays.

Introduction

One of the important facts which distinguishes vitrified salt glazed sewer pipe from other structural materials is that they have both a glaze and body which are resistant practically to all chemicals occurring in sewage and industrial wastes. The glaze produces upon the body an easily cleanable surface offering the least resistance to the flow of liquids through the pipes. It also seals up small body imperfections making the pipe more resistant to the penetration of liquids and gases. For sewer pipe it is therefore an advantage to have the glaze as thick as possible in addition to having a vitreous body.

In order to determine more thoroughly what the composition of a clay should be to take a salt glaze and at what temperature it should be glazed, a study is being made of the effects of different constituents in clays upon the ability of the clay to take a salt glaze at different temperatures. The types of glazes produced upon clays are dependent upon the chemical composition of the clay, since a salt glaze is formed by the melting of the outer surface of the pipe in combination with sodium compounds from the salt vapors. The salt glazing temperature also has an important influence upon the type of glaze produced as this may be too high or too low depending upon its chemical composition.

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[1] Published through the courtesy of The Eastern Clay Products Association and The Clay Products Association under whose auspices this work has been conducted as a part of their research program on the manufacture of clay sewer pipe.

[2] Senior Fellow, The Mellon Institute of Industrial Research, University of Pittsburgh, Pittsburgh, Pa.

In previous work, the writer[1] has shown that a high content of fine silica is desirable to produce good glazes, while high content of iron oxide and alumina may prevent a clay from taking a bright salt glaze. This report is limited to the results obtained in a study of the effects of variable lime content in clays upon their ability to take a glaze at different temperatures.

Experimental Methods

Two series of mixtures were studied in this investigation. The first was prepared with varying amounts of silica, alumina and lime and was practically free from iron oxide. The second series was prepared with these same constituents, but it contained approximately 5.32% iron oxide in terms of calcined weight in each case.

The mixtures were made by adding varying amounts of potter's flint, calcium carbonate, and iron oxide to a 1:1 Florida kaolin:Tennessee ball clay mixture. These were varied between the following limits:

	Series I	Series II
Alumina, Al_2O_3	10.22–40.50	9.70–38.90
Silica, SiO_2	53.12–88.55	51.10–84.16
Iron oxide, Fe_2O_3	0.38– 1.48	5.10– 5.44
Lime, CaO	0.16– 8.22	0.15– 7.32

Thirty-six mixtures for each series were prepared and the compositions of these in the calcined state are given in Tables I and II.

The raw mixtures were molded into $^1/_2$ x $^1/_2$ x $1^3/_4$ inch briquettes which were set in fire clay plaques, together with standard cones and were fired and salt glazed at cones 02, 3, 7 and 10 in commercial, coal-fired sewer pipe kilns. The glazes obtained on the briquettes were examined for brightness and color by means of the naked eye. The thickness of the portion of the surface which had become fused by the salt vapors was measured under a microscope.

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[1] "Clay Sewer Pipe Manufacture. II.—The Effects of Variable Alumina, Silica and Iron Oxide in Clays on Some of the Properties of Salt Glazes," *Jour. Amer. Ceram. Soc.*, **6**, 717–29(1923).

TABLE I—THE ALUMINA, SILICA, IRON OXIDE, AND LIME CONTENTS IN THE CALCINED MIXTURES OF SERIES I

	Al_2O_3	SiO_2	Fe_2O_3	CaO		Al_2O_3	SiO_2	Fe_2O_3	CaO
L 1	37.30	53.12	1.36	8.22	O 1	39.15	55.80	1.40	3.65
L 2	31.72	58.93	1.16	8.19	O 2	33.40	61.80	1.22	3.58
L 3	26.30	64.56	0.97	8.17	O 3	27.75	67.83	1.00	3.52
L 4	20.85	70.26	0.76	8.13	O 4	21.95	73.80	0.80	3.45
L 5	15.52	75.80	0.57	8.11	O 5	16.30	79.80	0.59	3.41
L 6	10.22	81.30	0.38	8.10	O 6	10.62	85.66	0.38	3.38
M 1	38.00	53.90	1.38	6.72	P 1	39.85	56.64	1.45	2.06
M 2	32.38	59.94	1.18	6.58	P 2	33.90	62.83	1.23	2.04
M 3	26.75	65.60	0.97	6.68	P 3	28.11	68.90	1.03	1.96
M 4	21.30	71.30	0.78	6.62	P 4	22.20	75.10	0.81	1.86
M 5	15.85	77.02	0.58	6.55	P 5	16.50	81.07	0.60	1.83
M 6	10.38	82.74	0.38	6.50	P 6	10.75	87.10	0.39	1.75
N 1	38.54	54.90	1.40	5.16	Q 1	40.50	57.44	1.48	0.58
N 2	32.90	60.81	1.19	5.10	Q 2	34.50	63.75	1.25	0.50
N 3	27.20	66.80	0.99	5.06	Q 3	28.55	70.00	1.04	0.41
N 4	21.60	72.60	0.79	5.01	Q 4	22.59	76.30	0.81	0.32
N 5	16.05	78.40	0.59	4.96	Q 5	16.72	82.43	0.61	0.24
N 6	10.50	84.20	0.38	4.92	Q 6	10.90	88.55	0.39	0.16

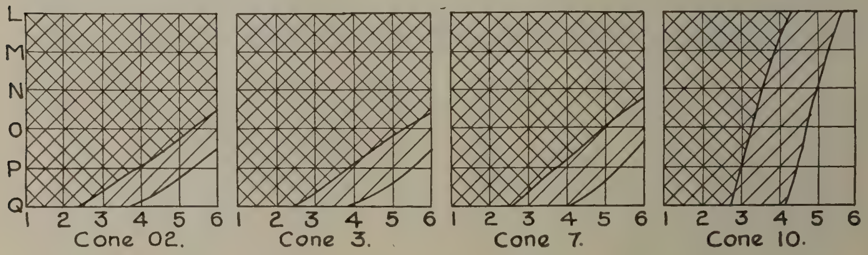
TABLE II—THE ALUMINA, SILICA, IRON OXIDE AND LIME CONTENTS IN THE CALCINED MIXTURES OF SERIES II

	Al_2O_3	SiO_2	Fe_2O_3	CaO		Al_2O_3	SiO_2	Fe_2O_3	CaO
R 1	36.20	51.10	5.38	7.32	U 1	37.70	53.60	5.42	3.28
R 2	30.80	56.58	5.34	7.28	U 2	32.24	59.20	5.36	3.20
R 3	25.50	61.96	5.30	7.24	U 3	26.65	64.90	5.33	3.12
R 4	20.25	67.33	5.22	7.20	U 4	21.15	70.55	5.24	3.06
R 5	15.00	72.70	5.18	7.12	U 5	15.67	76.16	5.18	2.99
R 6	9.10	78.10	5.10	7.10	U 6	10.25	81.70	5.14	2.91
S 1	36.70	51.90	5.39	6.01	V 1	38.35	54.40	5.34	1.91
S 2	31.40	57.30	5.36	5.94	V 2	32.65	60.14	5.37	1.84
S 3	25.90	63.02	5.24	5.84	V 3	27.11	65.80	5.32	1.77
S 4	20.55	68.44	5.20	5.81	V 4	21.50	71.56	5.25	1.69
S 5	15.32	73.75	5.17	5.76	V 5	15.90	77.30	5.20	1.60
S 6	9.95	79.25	5.10	5.70	V 6	10.46	82.86	5.14	1.54
T 1	37.25	52.72	5.42	4.62	W 1	38.90	55.10	5.44	0.56
T 2	31.70	58.40	5.35	4.55	W 2	33.10	61.06	5.37	0.47
T 3	26.25	63.94	5.29	4.52	W 3	27.41	67.90	5.30	0.39
T 4	20.90	69.43	5.23	4.44	W 4	21.75	72.67	5.26	0.31
T 5	15.49	74.94	5.17	4.40	W 5	16.12	78.10	5.15	0.23
T 6	10.12	80.42	5.12	4.33	W 6	10.55	84.16	5.14	0.15

Experimental Results

The Effect of Varying Lime Contents and Salt Glazing Temperatures upon the Glossiness of Salt Glazes

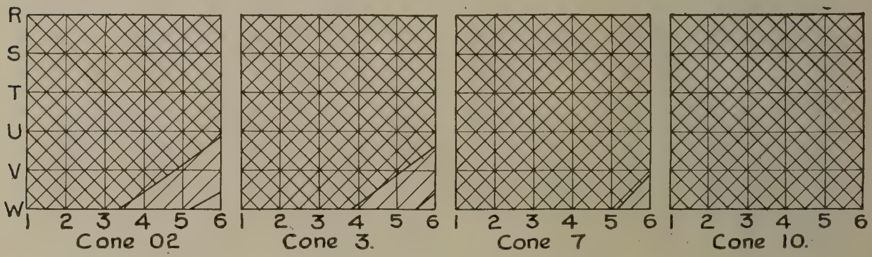
The influence of different lime contents and salt glazing temperatures upon the glossiness of salt glazes is shown graphically in Figs. 1, 2 and 3. Salt glazing clays at higher temperatures will produce much brighter glazes on low iron clays containing a high content of lime than when they are glazed at low temperatures. At low temperatures a small percentage of lime (1.00%) will prevent a clay which would otherwise take a good salt glaze from taking a bright glaze.



	SiO_2	Al_2O_3	CaO	Fe_2O_3
L1	53.12	37.30	8.22	1.36
L6	81.30	10.22	8.10	0.38
Q1	57.44	40.50	0.58	1.48
Q6	88.55	10.90	0.16	0.39.

▭ Bright glazes. ▨ Semi Matt glazes. ☒ Matt glazes.

FIG. 1.—The influence of lime in clays on their ability to take a glaze at different temperatures.



	SiO_2	Al_2O_3	CaO	Fe_2O_3
R1	51.10	36.20	7.32	5.38
R6	78.10	9.70	7.10	5.10
W1	55.10	38.90	0.56	5.44
W6	84.16	10.55	0.15	5.14

▭ Bright glazes. ▨ Semi Matt glazes. ☒ Matt glazes.

FIG. 2.—The influence of lime in clays high in iron oxide on their ability to take a glaze at different temperatures.

The results shown in these diagrams can be approximately represented by means of the following empirical formula which was derived from the data of this and previous work:

$$g_1x_1 + g_2x_2 + g_3x_3 + g_4x_4 = 100\,G \qquad (1)$$

x_1, x_2, x_3 and x_4 represent the percentages of alumina, silica, iron oxide and lime, respectively, in the clay in terms of the calcined weight. g_1, g_2, g_3 and g_4 represent the gloss factors for alumina, silica, iron oxide and lime. In previous work,[1] it was found that g_1 and g_2 were -1.00 and $+0.376$, between 1110° and 1330°C. g_3 varies as follows with the salt glazing temperature as is represented by the following equation where T is the salt glazing temperature in degrees Centigrade.[2]

$$g_3 = -1.885 - 0.385 - (1.01253)^{(T-1110)} \qquad (2)$$

In this investigation it was found that g_4, for lime, varied from -8.70 to -1.91 depending upon the salt glazing temperature. This factor was found to be -8.70 at cone 02, -8.16 at cone 3, -7.10 at cone 7 and -1.91 at cone 10 (see Fig. 3).

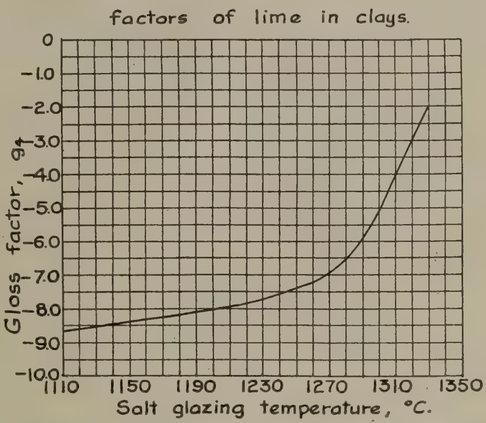


Fig. 3.—The influence of different salt glazing temperatures upon the gloss factors of lime in clays.

The value g_4 may be calculated for different temperatures by means of the following formula in which T represents the salt glazing temperature in degrees Centigrade:

$$g_4 = -1.91 - 2.117\,(1330 - T)^{0.219} \qquad (3)$$

The observed values for g_4 and those calculated by equation 3 are given below:

Temperature, °C	Observed g_4	Calculated g_4
1110	−8.70	−8.81
1190	−8.16	−8.16
1270	−7.10	−7.11
1330	−1.91	−1.91

G in equation 1, represents the gloss factor of the glaze produced with a clay and increases in proportion to the brightness and smoothness of the glaze. When G is greater than 0, the clay will produce a bright glaze provided it is fired under conditions similar to those under which the test pieces were fired.

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[1] "Clay Sewer Pipe Manufacture. II," *loc. cit.*

[2] "Clay Sewer Pipe Manufacture. IV.—The Influence of Different Salt Glazing Temperatures upon the Color and Gloss of Glazes Obtained on Clays with Varying Silica, Alumina, and Iron Oxide Contents," *Jour. Amer. Ceram. Soc.*, **7** [6], 411 (1924).

When G is between -0.1337 and 0, the glazes will be semi matt and when below -0.1337 they will be matt.

By substituting the different values for g_1, g_2, g_3 and g_4 in equation 1, this becomes as follows:

$$-1.00x_1 + 0.376x_2 - [1.885 + 0.385(1.01253)^{(T-1110)}]x_3 - [1.91 + 2.117\,(1330-T)^{0.219}]x_4 = 100\ G \qquad (4)$$

The tendency for lime to prevent clays from taking a bright salt glaze at low temperatures is probably due to the high combining temperature of sodium compounds with lime and also to the divitrification of the glazes in cooling due to the presence of lime.

The Effect of Varying Lime Contents on the Color of Glazes Obtained on Ferriferous Clays When Glazed at Different Temperatures

In Table III, and Fig. 4, are shown the effects of varying lime contents on the color of glazes obtained on ferriferous clays when glazed at different temperatures under the conditions of these tests. The high lime and high silica clays produced greenish yellow colors appearing very similar to those produced by scum on sewer pipe. This effect is most pronounced at high temperatures, cone 7 and 10, while at the lower temperatures, cone 02 and 3, the colors produced were about the same as those obtained on lime—free bodies as is represented by the following equation:[1]

$$10.3x_1 - 2.65x_2 + [14.6 + 54.1(1.0066)^{(T-1110)}]x_3 = 100\ \mathrm{C} \qquad (5)$$

x_1, x_2 and x_3 represent the percentages of alumina, silica and iron oxide, respectively, while C represents the ability of the clay to produce brown glazes. If C is between 4.75 and 8.2, mahogany colors are produced and when above 8.2, dark brown to black glazes are obtained.

At cone 7 and above, however, the above equation does not hold for the glazes high in lime and silica. As the lime and silica contents are increased in these, there is a gradual change from the brown to a disagreeable greenish yellow color, evidently due to the formation of compounds of this color from lime, iron oxide, alumina and silica together with sodium oxide. The tendency for this yellow color to form at cone 7 on clays containing 5.32% iron oxide, in terms of calcined weight, may be represented by the following formula:

$$a_1x_1 + a_2x_2 + a_4x_4 = 100\ A \qquad (6)$$

---

[1] "Clay Sewer Pipe Manufacture. IV," *loc. cit.*

x_1, x_2 and x_4 represent the percentages of alumina, silica and lime, respectively. a_1, a_2 and a_4 represent the greenish yellow color factors, which were found to be $-1.00 + 0.053$ and $+2.68$ for alumina, silica and lime, respectively. When A is above 0, the glaze will have a greenish yellow color instead of the brown color within the limits in composition as used in this investigation.

The Effects of Varying Lime Contents and Salt Glazing Temperatures upon the Thickness of the Translucent Surface

In examining the glazes under the microscope by letting a 60-watt electric light shine through the specimen from beneath at an angle of 45°, it was found that a certain portion of the outer surface became translucent. This translucent portion included some of the body underneath the glaze as well as the glaze. The thickness of this portion of the surface may be used as a measure of the depth to which the salt glazing action has penetrated into the body.

Measurements were made of the thickness of these translucent portions in order to determine the effects of lime and salt glazing temperature upon the same.

It was found that increasing the lime and silica contents and raising the salt glazing temperatures increased the thickness of the translucent portion (see Table III). There is no close relation between the brightness of the glazes and the thickness of the translucent portion. On many high lime clays, the thickness of this portion is much greater than that of some low lime bright glazes, although the high lime glazes are dull. This dullness is evidently due to a devitrification in many cases caused by the presence of lime.

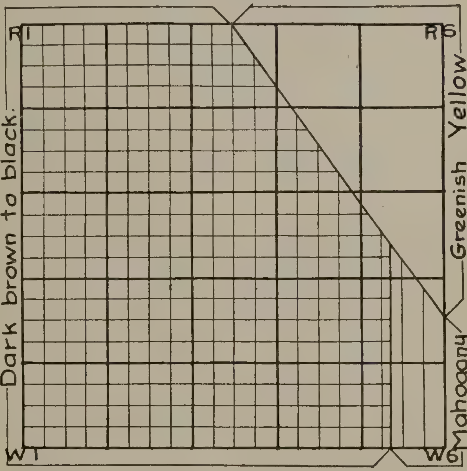

FIG. 4.—The influence of lime in clays containing 5.32% iron oxide upon the color of salt glazes obtained at cone 7.

TABLE III—THE THICKNESS OF THE TRANSLUCENT SURFACES ON THE CLAYS AFTER SALT GLAZING AT DIFFERENT TEMPERATURES

	Cones					Cones			
No.	02 Inches	3 Inches	7 Inches	10 Inches	No.	02 Inches	3 Inches	7 Inches	10 Inches
L 1	0.0056	0.0067	0.0073	0.0073	O 1	0.0056	0.0056	0.0070	0.0070
L 2	0.0056	0.0084	0.0084	0.0098	O 2	0.0056	0.0056	0.0070	0.0084
L 3	0.0070	0.0098	0.0098	0.0126	O 3	0.0056	0.0070	0.0084	0.0084

TABLE III (*continued*)

THE THICKNESS OF THE TRANSLUCENT SURFACES ON THE CLAYS AFTER SALT GLAZING AT DIFFERENT TEMPERATURES

	Cones					Cones			
	02	3	7	10		02	3	7	10
No.	Inches	Inches	Inches	Inches	No.	Inches	Inches	Inches	Inches
L 4	0.0070	0.0098	0.0112	0.0155	O 4	0.0070	0.0070	0.0084	0.0098
L 5	0.0089	0.0112	0.0126	0.0169	O 5	0.0070	0.0084	0.0098	0.0098
L 6	0.0098	0.0126	0.0169	0.0196	O 6	0.0070	0.0084	0.0098	0.0112
M 1	0.0056	0.0056	0.0070	0.0070	P 1	0.0056	0.0056	0.0070	0.0070
M 2	0.0056	0.0070	0.0070	0.0034	P 2	0.0056	0.0056	0.0070	0.0070
M 3	0.0070	0.0084	0.0084	0.0098	P 3	0.0056	0.0070	0.0070	0.0084
M 4	0.0070	0.0084	0.0098	0.0112	P 4	0.0070	0.0070	0.0084	0.0084
M 5	0.0084	0.0098	0.0112	0.0126	P 5	0.0070	0.0084	0.0084	0.0098
M 6	0.0084	0.0098	0.0126	0.0142	P 6	0.0070	0.0084	0.0084	0.0098
N 1	0.0056	0.0056	0.0070	0.0070	Q 1	0.0056	0.0056	0.0070	0.0070
N 2	0.0056	0.0070	0.0084	0.0084	Q 2	0.0056	0.0056	0.0070	0.0070
N 3	0.0056	0.0070	0.0084	0.0084	Q 3	0.0056	0.0056	0.0070	0.0070
N 4	0.0070	0.0084	0.0084	0.0098	Q 4	0.0070	0.0070	0.0084	0.0084
N 5	0.0070	0.0084	0.0098	0.0112	Q 5	0.0070	0.0070	0.0084	0.0084
N 6	0.0070	0.0084	0.0112	0.0126	Q 6	0.0070	0.0070	0.0084	0.0084

Varying the Lime Content and Salt Glazing Temperatures as Means of Improving the Quality of Sewer Pipe Glazes

By means of equation 1, it is possible to calculate the amount of lime permissible in clays containing varying amounts of iron oxide, when glazed at different temperatures in order to obtain bright and semi matt glazes. Some of the results calculated by means of this equation are given in Table IV.

Both lime and iron oxide prevent clays from taking a bright glaze when present above a certain amount. Lime is most harmful at low temperatures, while iron oxide is most injurious at high temperatures.

Low iron and high lime clays take the brightest glaze at high temperatures, as is shown by the higher content of lime permissible to produce bright and semi matt glazes at high temperatures as compared with that permissible at low temperatures (see Table IV). Low lime and high iron clays on the other hand should be fired at as low temperatures as possible in order to produce the smoothest glazes.

Summary and Conclusions

The following conclusions were drawn from the results of this investigation. These tests were conducted in commercial kilns and therefore apply fairly accurately when the pipe are fired and salt glazed under normal conditions within the limits of composition as was used in this investigation. If the kiln is fired extremely reducing, the glazes obtained would be similar to those obtained at higher temperatures. If fired strongly oxidizing, they would approach those produced at lower temperatures in their properties.

1. A low percentage of lime in clays (1.00%) will prevent them from taking a bright glaze at low temperatures.

2. High lime clays can best be glazed at high temperatures providing the iron oxide content is not high (above 3.5%).

TABLE IV—THE MAXIMUM PER CENT OF LIME IN CLAYS PERMISSIBLE TO OBTAIN BRIGHT AND SEMI MATT GLAZES ON CLAYS WITH VARYING IRON OXIDE CONTENTS AT DIFFERENT TEMPERATURES

		0% Fe_2O_3			3% Fe_2O_3			5.32% Fe_2O_3		
Salt glazing temp. cones	Appearance of glaze	$\frac{\% SiO_2}{\% Al_2O_3} = 2$	$\frac{\% SiO_2}{\% Al_2O_3} = 4$	$\frac{\% SiO_2}{\% Al_2O_3} = 6$	$\frac{\% SiO_2}{\% Al_2O_3} = 2$	$\frac{\% SiO_2}{\% Al_2O_3} = 4$	$\frac{\% SiO_2}{\% Al_2O_3} = 6$	$\frac{\% SiO_2}{\% Al_2O_3} = 2$	$\frac{\% SiO_2}{\% Al_2O_3} = 4$	$\frac{\% SiO_2}{\% Al_2O_3} = 6$
Cone 02	Bright	..[1]	1.15	2.02	..[1]	1.06	1.88	..[1]	1.01	1.77
	Semi matt	0.59	2.78	3.52	0.54	2.58	3.36	0.47	2.53	3.28
Cone 3	Bright	..[1]	1.22	2.15	..[1]	1.11	1.96	..[1]	1.03	1.82
	Semi matt	0.62	2.84	3.75	0.54	2.72	3.57	0.47	2.64	3.42
Cone 7	Bright	..[1]	1.40	2.46	..[1]	1.19	2.13	..[1]	1.05	1.83
	Semi matt	0.72	3.36	4.30	0.55	3.09	3.92	0.42	2.90	3.68
Cone 10	Bright	..[1]	5.02	8.57	..[1]	3.82	6.55	..[1]	2.91	4.99
	Semi matt	2.66	11.65	14.95	1.64	10.45	10.00	0.85	9.55	11.40

3. The effects of varying lime contents and salt glazing temperatures upon the brightness of salt glazes produced on clays containing iron oxide may be predicted by calculating G in the following equation:

$$-1.00x_1 + 0.376x_2 - [1.885 + 0.385(1.01253)^{(T-1110)}]x_3 - [1.91 + 2.117(1330-T)^{0.219}]x_4 = 100\,G$$

When G is greater than 0, the glaze will be bright, when between -0.1337 and 0 it will be semi matt and when below -0.1337 it will be matt.

4. High lime and high silica clays produce greenish yellow glazes at cone 7 and above in clays containing 5.32% iron oxide. The tendency of lime to produce these greenish yellow colored glazes may be represented by the following equation:

$$-1.00x_1 + 0.053x_2 + 2.68x_4 = 100\ A$$

When A is above 0, the glaze will have a greenish yellow color.

5. Increasing the lime content and raising the salt glazing temperatures increased the thickness of the glassy and fused surface of the clays due to the action of salt vapors.

In conclusion the writer wishes to acknowledge his indebtedness to Dr. E. W. Tillotson for help during the progress of this work.

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[1] The alumina content is too high to produce bright glazes.

THE PROBLEM OF HEAT ECONOMY IN THE CERAMIC INDUSTRY.—III[1]

By Willi Cohn

The substances already tested, especially clay substance, feldspar and quartz, are primarily representative of the raw materials which find use in ceramic industries and to which almost all compounded bodies and materials used in the industry may be referred. Once the behavior of these primary substances during heating is known we shall be in a position to calculate directly from them the behavior of the compounded materials.

Given a substance A which at temperature t shows a heat variation of $+X$ calories; let a second substance B at the same temperature t show a heat variation of $-Y$ calories.

Now let a definite mass be composed of a percentages of A and of b percentages of B. If this compound mass then be heated to temperature t, we can calculate the heat variation Z according to the formula, by assuming a purely additive behavior of the components:

$$Z = \frac{1}{100}\,(a(+X) + b(-Y))$$

In order to test the correctness of this formula we examined a number of ceramic materials employed in the industries and determined their behavior quantitatively during the heating process. The results are given below. Besides the values found directly, we give also the values calculated on the basis of the above formula. There appeared—it may be said in advance—a fair agreement between the values found by the two methods.

If the behavior of the several components in their thermal relations is known, and if the per cent composition of the test material is known, we can calculate in advance the values of the heat variations that may be expected.

If, however, the behavior of the several components in their thermal relations is known quantitatively, then the composition of the mass, in percentages, can be determined as follows:

Given the substance A which at temperature t shows a heat-change of $+X$ calories, let the same substance at temperature t_1 show a heat-change of $-Z$ calories, let a second substance B, at temperature t show a heat-change of $+Y$ calories; let a substance C during heating show no heat-change whatever.

Let us assume we had determined that a mass, which could be composed of A, B, C, possesses a heat-change of $+U$ at temperature t, and at temperature t_1 of $-V$ calories. We should then have to determine what is the per cent share of the several components of this mass.

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[1] Parts I and II of this paper have appeared in *Jour. Amer. Ceram. Soc.*, **7** [5], 359; **7** [6], 475. Part III concludes the series.

The reaction $+U$ taking place at temperature t permits us to draw conclusions with reference to the component A as well as to B. We therefore can formulate an equation with two unknowns having the same formula as the equation on page 548. The heat-change of $-V$ calories occurring at temperature t_1 can only be referred to the component A. Accordingly we can establish the second equation which is needed for the solution of the first.

The determination of the per cent share of the third component is obtained by subtracting the two other percentages from 100.

Porcelain Mass—Unfired

We tested some unfired porcelain mass from the Government Porcelain Factory at Berlin. Its composition was: clay substance 55.0, quartz 22.5, and feldspar 22.5%.

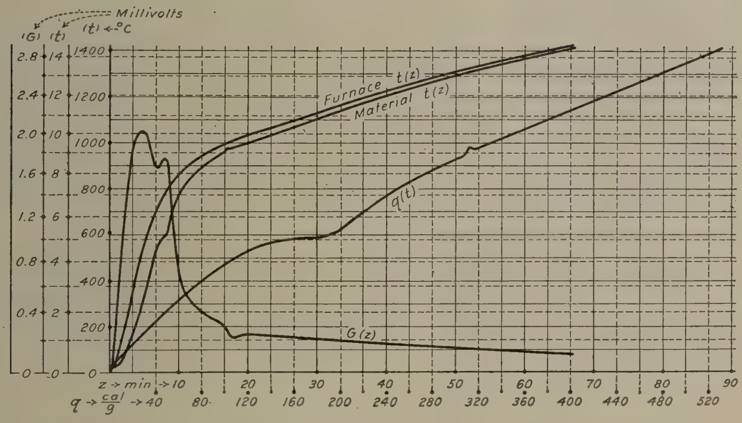

FIG. 32.

The temperature-time curve (Fig. 32) shows particularly well the reactions in the clay substance, while the reactions in the other components of the mass played but a subordinate role. The following values resulted:

1. Endothermal Reactions

The endothermal reaction caused by the splitting off of water in chemical combination, as well as by the transformation of the quartz occurring at the same temperature, and reaching its maximum at about 575°C, was clearly observed. The q-t curve for this showed: 53.1 ±2 cal./g.

The calculation with the aid of the formula on page 548 showed the heat-change of the clay substance to be 51.70 cal./g and of quartz 0.98 cal./g, respectively, or a total of 52.68 cal./g. The two values thus agreed fairly well within the limits of error of the experiment.

2. Exothermal Reaction

The exothermal process appeared at about 950°C, having been caused by the clay substance. The loop showing for the kaolins, etc., appeared to be concentrated at one point. The value of the reaction was −8.8 ±0.3 cal./*g*. Calculating the values on the basis of the formula mentioned repeatedly the heat-change for the process showed −9.08 cal./*g*.

3. Other Reactions

The gradual endothermal reaction—the significance of which has been pointed out on page 548—was also clearly observed. The rest of the reactions whose occurrence at higher temperatures in porcelain firing is assumed, could not be recognized from the curves here given since these reactions are of slow progress.

Porcelain Mass—Fired

The same kind of mass—of a composition indicated above—was then tested. The heating curve ran uniform, indicating no reaction.

Here again appeared the regularity previously observed, *viz.*, that fired material has a higher specific heat than unfired material. Of course this applies only to that range of temperature where no reactions occur within the mass. Where there are any reactions, these different heat-changes, occurring between a low initial and the subsequent temperatures, are included in the mean specific heat.

Former Tests

With a mixture calorimeter Harker[1] determined the mean specific heat of fired porcelain and established the following values between an initial temperature of 15°C and the following temperatures:

Temp. °C	912	958	1075
c_m	0.2582	0.2563	0.2539

These values are striking in that they—contrary to all similar known tests—show a decrease of specific heat with an increasing temperature; a condition that seems very improbable.

Steger[2] with the aid of a copper calorimeter, from an initial temperature of 20°C, found that fired porcelain at 200°C has the following value: $c_m = 0.202$. This coincides very well with the values found by us.

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[1] J. A. Harker, "The Specific Heat of Iron at High Temperatures," *Phil. Mag.*, **6**, 10 (1905).

[2] W. Steger, "Über die mittlere spezifische Wärme einiger keramischer Massen in zwei verschiedenen Temperaturbereichen; Über die spezifische Wärme feuerfester Erzeugnisse," *Sil.-Z.* (1914).

Porcelain Glaze—Unfired

In order to obtain a complete survey of all the processes entering into the firing of porcelain, we tested a raw glaze mixture with the following results:

We tested the usual hard porcelain glaze from the Government Porcelain Factory at Berlin, intended for Seger cone 16 (1460°C). The temperature-time curve (Fig. 33) showed various reactions. The detailed results are as follows:

1. Endothermal Reaction

The splitting off of water in chemical combination as well as the transformation of quartz occurring at the same temperature could be well observed at 575°C. The value of the heat-change that occurred was 16.4 ±0.5 cal./*g*.

2. Exothermal Reaction

Between 900 and 1000°C there occurred a reaction which differed from any in previously tested materials. While in other cases the reaction took place almost immediately, here it extended for a considerable period of time. Moreover, it appeared to be composed of several separate reactions.

This reaction is probably caused primarily by the clay substance present in the mass, which as we know at this temperature shows an exothermal reaction. In addition to this, especially on the *G-z* curve, there was noticeable a frequent fluctuation of the temperature of the mass. In all probability this indicates some decomposition processes of the carbonate of lime present in the mass, as well as a decomposition of magnesite; both of which occur endothermally. The heat-change occurring at this temperature totaled 12.3 ±0.4 cal./*g*.

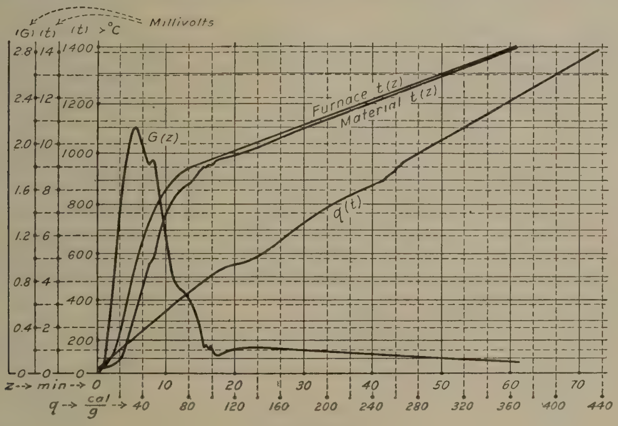

Fig. 33.

Porcelain Glaze—Fired

Porcelain glaze of the same composition as the above-mentioned unfired glaze—fired with Seger cone 16 (1460°C), showed a completely uniform heating curve without any reactions.

Whiteware—Unfired

To further test the formula stated on page 548, we submitted to test some whiteware material of the following composition: clay substance 50%, quartz 45%, and feldspar 5%. The temperature-time curves and the temperature-heat curves showed the same reactions as those of other unfired materials under test. The detailed results:

1. Endothermal Reaction The endothermal reaction caused by the splitting off of water in chemical combination, as well as that caused by the transformation of quartz at the same temperature—which reached its maximum at about 575°C—could be clearly seen and showed this value: 48.9 ± 2 cal./*g*. The calculation of this value showed the heat-change of clay substance to be 47.00 cal./*g* and of quartz 1.96 cal./*g*, respectively, or a total of 48.96 cal./*g*. These two values agreed fairly well.

2. Exothermal Reaction The exothermal reaction occurring at about 950°C, caused by the clay substance, was −7.9 ± 0.3 cal./*g*.

The calculation of this value resulted in −8.25 cal./*g*.

Whiteware—Fired

The same kind of whiteware substance of the above-mentioned composition and fired with Seger cone 9 (1280°C) was next subjected to test.

In consequence of the large quartz content the reversible transformation of quartz, setting in at 500°C, could also be clearly distinguished with this fired material. The several results:

1. Endothermal Reaction The transformation of quartz, occurring at 575°C, showed a heat change of 1.7 ± 0.1 cal/*g*. The value ascertained from the composition of the mass is 1.96 cal./*g*.

Here also the mean specific heat of the fired material was higher than that of the unfired.

Saarau Fire Clay—Unfired

The test material was composed of clay substance 87%, quartz 9%, and feldspar 4%. The temperature-time curve, as well as the temperature-heat curve, showed the usual course and gave the following values:

1. Endothermal Process To split off the water held in chemical combination, also to transform the quartz at a temperature of 575°C, required 81.2 ± 3 cal/*g*. The calculation of the value from the components showed the heat-change of clay substance to be 81.78 cal./*g* and of quartz 0.39 cal./*g*, respectively, or a total of 82.17 cal./*g*. These two values agree well.

2. Exothermal Reaction The exothermal process caused by the clay substances, and occurring at about 950°C, show: −13.8 ± 0.4 cal./*g*.

Calculating this value we have −14.35 cal./*g*.

Fire Clay—Fired

In recent times a large number of fire-clay materials have been subjected to tests. The best known were made in the Government Testing Bureau (Materialprüfungsamt) at Berlin by Heyn, Bauer and Wetzel.[1] These investigators made use of the water calorimeter according to the method of mixtures.

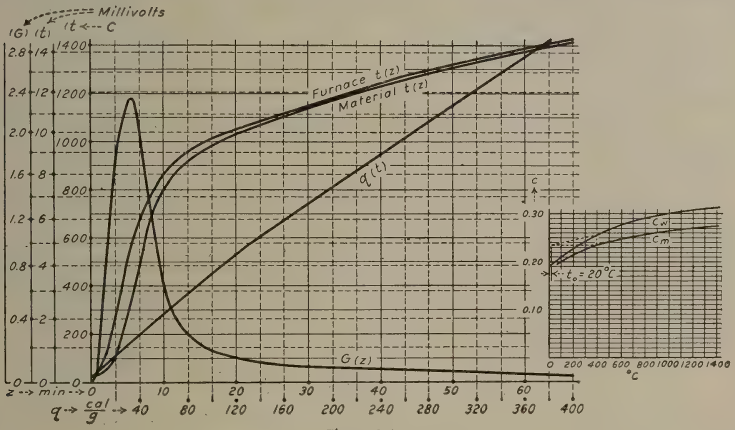

FIG. 34.

Inasmuch as the fire-clay materials used in industry show quite varying composition, the writer requested Professor Bauer to place at his disposal, for testing, the material previously investigated. We thereby hoped to obtain values which might be compared with the results already published. Professor Bauer was kind enough to grant the request and furnished the test materials.

At the same time the investigation of fire-clay bodies whose behavior was already known, served as a check on the new method for determining specific heat and heat-changes.

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[1] E. Heyn, O. Bauer, and E. Wetzel, "Untersuchungen über die Wärmeleitfähigkeit feuerfester Baustoffe," Mitteil. aus d. Königl. Materialprüfungsamt., 1914, 2/3.

The tests made with the several materials showed a maximum deviation of ±2% from the previously known values; this then comes within the range of error. As a test-sample for this investigation we chose the body *BC;* Figure 34 shows the curves obtained as well as the specific heat determined therefrom. See also Tables I and II.[1]

Fire-clay Body BC—Fired

According to the specifications of the firm which furnished this material, the composition of the body was: SiO_2 about 57%, and Al_2O_3 40%. The values obtained from the temperature-time curve and from temperature-heat curve are given in Tables I and II.

In order to make possible a direct comparison with the values given by Heyn, Bauer and Wetzel,[2] we used the method indicated in Fig. 34 for determining graphically true specific heat from the mean specific heat. The following table gives the values ascertained as well as the findings of Heyn, etc., for purposes of comparison:

Temp. °C	200	400	600	800	1000	1200	1400
c_w	0.227	0.254	0.277	0.290	0.301	0.309	0.313
c_w(Heyn)	0.225	0.250	0.272	0.287	0.298	0.305	

From these figures may be seen how well the results obtained by two different methods agree.

In order to make a test, similar to those with the previous materials, on a fire clay in both the raw and the fired state we fired and tested some Saarau clay referred to on page 552. The results were:

Saarau Fire Clay—Fired

The fired clay showed a perfectly uniform temperature-time curve with no reactions occurring. Results in Tables I and II.

These values differ but little from the values of fired fire clay materials as ascertained by Heyn, Bauer and Wetzel.[3]

Clay from Halle

We tested some lean clay from Halle used in the Government Porcelain Factory at Berlin for comparison with the fat Zettlitz kaolin, the test-results for which were given on page 478,[4] etc. Its composition was: clay substance 65%, quartz 34%, and feldspar 1%. The known reactions appear on the temperature-time curve as well as on the temperature-heat curve. The following values resulted:

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[1] *Jour. Amer. Ceram. Soc.,* **7** [6], 482-83 (1924).

[2] Heyn, Bauer and Wetzel, *loc. cit.*

[3] *Ibid.*

[4] *Jour. Amer. Ceram. Soc.,* **7** [6], 478.

1. Endothermal Reaction

The endothermal reaction caused by the splitting off of water in chemical combination and by the transformation of the quartz at about 575°C was 62.2 ± 2 cal./*g*. The calculation of this value from the components showed the heat-change of clay substance to be 61.10 cal./*g*. and of quartz 1.48 cal./*g*., respectively, or a total of 62.58 cal./*g*.

2. Exothermal Reaction

At about 950°C the exothermal process caused by the clay substance shows up; it was −11.0 ± 0.3 cal./*g*. The calculation of this value is −10.73 cal./*g*.

Summary of the Results

The tables on pages 482 and 483[1] give the summary of figures which resulted from our investigations.

Table I indicates the quantity of heat required for heating 1 g. of the given substance, expressed in ("small") calories, as well as the amount of heat-changes occurring during the heating process.

Table II shows the mean specific heat calculated from Table I, between 20°C and the subsequent temperatures. These values include the values of the heat-changes, wherever they occur.

Application of the Test-Results

On the basis of our determinations of specific heat and heat-changes for ceramic materials, heretofore almost unknown, we are enabled to state actually what quantity of heat is required for the firing of the different wares. We can now make heating charts, provided the other requisite values have been determined by the usual measurements.

Frequent attempts at constructing such charts have been made before. We would mentioned as foremost the work by Bleininger,[2] Gelstharp,[3] Wilson, Holdcroft and Mellor,[4] Reutlinger,[5] and lastly by Spindler.[6]

The weakness of all of these charts lies in the fact that the quantity of heat actually required for firing the materials had only been estimated. This present work is intended to bridge this gap.

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[1] *Jour. Amer. Ceram. Soc.*, **7** [6], 482–83.

[2] A. V. Bleininger, "A Study of the Heat Distribution in Four Industrial Kilns," *Trans. Amer. Ceram. Soc.*, **10**, 412 (1908).

[3] F. Gelstharp, "Heat Balance of a Plate Glass Furnace," *Trans. Amer. Ceram. Soc.*, **2**, 621 (1910); Ref. *Sprechsaal* (1911).

[4] Wilson, Holdcroft and Mellor, "The Specific Heats of Fire Bricks at High Temperatures," *Trans. Ceram. Soc.* (English) (1912–13).

[5] E. Reutlinger, "Über die Brandführung in Porzellanrund-und Tunnelöfen," *Ber. d. Deutsch. Keram. Ges.*, **3**, 3 (1922).

[6] M. Spindler, "Die Feuerführung und Wärmewirtschaft des Tunnelofens," *Ber. d. Deutsch. Keram. Ges.*, **3**, 4 (1922).

Heating Chart for Porcelain Kiln

As a sample for making a chart we shall give a heating chart for a commercial kiln—tested by Wilson, Holdcroft and Mellor[1] which has been used for initial firing of china ware. This chart gives only an approximate index for the action of such a kiln and makes no claims as to completeness or accuracy.

The type referred to was a round kiln containing: saggers 18.288 kg., ware 4.318 kg., and flint (for packing) 2.286 kg. The temperature for firing was 1200°C; fuel consumption 9398 kg. coal of 7500 Cal./*kg* minimum heat value.

Since the composition of the porcelain so fired was not known, we use as basic the values known for Berlin hard porcelain.

On the basis of Table I we find the following consumption of heat—starting with room temperature—for attaining 1200°C for the several materials (per 1 kg. each) in the kiln:

Saggers (fired fire clay)	315.0 Cal./*g*.
Ware (raw porcelain)	428.4
Flint (quartz, extrapolated)	348.8

The firing of the kiln contents would then require:

Saggers	5,760,720.0 Cal.
Ware	1,849,831.2
Flint	797,356.8
Total	8,407,908.0 Cal.

The actual coal consumption of 9398 kg. corresponds to 70,485,000.0 Cal.

Thus of the inducted heat 11.95% is utilized for heating the contents of the kiln. The firing of the wares requires of this inducted quantity of heat only 2.63%.

The result shows at what low efficiency a large number of kilns employed in ceramic industry are functioning.

This heating chart—as already stated—gives only approximate values. An example of a complete investigation of this sort may be found in the work of Spindler.[2]

Utilization of Heat in Ceramic Kilns

The following is a calculation, on the basis of the figures of Spindler,[3] of the percentage of fuel actually utilized during porcelain firing in various types of kilns.

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[1] Wilson, Holdcroft and Mellor, *loc. cit.*

[2] M. Spindler, *loc. cit.*

[3] *Ibid.*

Requisite are (coal, 6500 Cal./*kg* heat value):

For round kilns	3.5 to 2.8 kg. fuel per kg. net kiln charge
For gas compartment kilns	2.5 to 2.0 kg. fuel per kg. net kiln charge
For tunnel kilns	1.4 to 0.7 kg. fuel per kg. net kiln charge

Theoretically the fuel consumption for obtaining a temperature of 1400°C for raw porcelain body (Table I) is 527.7 Cal./*kg*. This value corresponds to 0.081 kg. coal of 6500 Cal./*kg* heat value. The various types of kilns therefore utilize:

Circular kilns	2.32 to 2.89% of the fuel used
Gas compartment kilns	3.24 to 4.05% of the fuel used
Tunnel kilns	5.79 to 11.57% of the fuel used

These figures give a fair survey of the functioning of the different types of kilns in actual use, and likewise show that the tunnel kiln works more economically than the other two types.

Conclusions

The principal results of the present investigations are:

1. The previously known methods concerned with determining of the bases for the investigation of heat economy in ceramic industry have been assembled and critically discussed.

2. A new method has been developed for determining directly specific heat as well as heat-changes in solid bodies, a method which can also be employed with very high temperatures. This is based on the calibration of an electric furnace with the help of a substance whose behavior is known at the temperatures concerned.

3. The application of this new method has been carried out with raw materials commonly used in ceramic industry, as well as with a number of bodies generally used in that industry. It has been shown that probable heat-changes in compounded bodies can be determined fairly accurately from the heat-changes of the raw materials, provided their composition is known.

It has been shown that, inversely, on the basis of heat-changes in compounded bodies, measured quantitatively, their composition may be determined.

4. A heating chart has been made on the basis of the results obtained.

5. A summary has been made of the utilization of heat by the various types of kilns in use in ceramic industry.

Finally, I would not omit expressing my cordial thanks to the Director of the Chemo-Technical Testing Bureau in the Government Porcelain Works at Berlin, Prof. Dr. Rieke, for his kindly help and constant encouragement during this investigation. Likewise my gratitude extends to

Professor Dr. Volmer, the Director of the Institute for Physical Chemistry and Electro-Chemistry at the Technische Hochschule, Berlin, for his cordial interest. I also make grateful acknowledgment of assistance from individuals and firms which have so kindly supported this investigation by supplying the requisite materials.

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COMPARATIVE CRAZING AND CHIPPING OF WET AND DRY PROCESS CAST IRON ENAMELS[1]

By J. T. Robson[2]

ABSTRACT

Heat shock tests are run on commercial samples of cast iron stove parts enameled by both the wet and dry process. These enamels applied by the wet process are much more resistant to temperature change than those enamels applied by the dry process.

Crazing and chipping of the cast iron parts of enameled stoves is one of the chief difficulties with which the manufacturer must contend. In spite of the fact that such stoves bear labels cautioning the user not to rub the enameled parts with a damp cloth or moisten them in any way while hot, there seems to be a natural inclination to either forget or disregard such warnings after the stove has been in use for a short while. This often results in crazing or chipping of the enamel with the result that such pieces become unsightly in appearance and in many cases must be renewed by the manufacturer of the stove.

It is, therefore, of importance to know whether or not there is any difference in resistance to crazing or chipping in those enamels applied by the wet and dry processes. With this view in mind, three samples each of main oven front extension castings, measuring approximately 12 x $1^5/_8$ x 1 inch (see Fig. 1), were sent to different plants and enameled by them. These were labeled as follows: Those by the wet process, Nos. 1, 2, 3 and 4. Samples 1, 2 and 3 were enameled at the same plant but using different enamels. Samples 5, 6, 7 and 8 were enameled by the dry process. Nos. 5 and 6 were enameled with the same enamel which was applied heavy on No. 5 and light on No. 6.

Crazing and Chipping Test

Two pieces each of the eight different enamels, labeled *a* and *b*, were heated in an electric furnace and then immediately plunged into water at a temperature of 76°F. The temperature of the electric furnace up through 650°F was determined by a thermometer, the bulb of which was in contact with the enamel. Above 650°F, the temperature was determined by means of a thermocouple. After remaining in water until cool, the pieces were removed, dried with a towel and examined very carefully by the eye and red ink absorption, for crazing marks and chipping. After each test up to 500°F, the furnace was allowed to cool. The pieces were then again charged and the furnace was brought up to the given temperature. Above 500°F the furnace was not allowed to cool down more than about 100°F between each test. After the pieces had chipped or crazed sufficiently to render them unfit for use, they were no longer heated except where noted in the data.

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[1] Listed on program at Atlantic City Meeting, Feb., 1924 (Enamel Division).

[2] Based on work done with The Tappan Stove Co., Mansfield, Ohio.

The condition of one each of the samples after testing is shown in Fig. 1.

The temperatures to which the different enamels could have been heated without chipping or crazing sufficiently to be apparent are as follows:

No.	(*a*)	(*b*)
1	900°F	900°F
2	400	550
3	400	550
4	500	500
5	200	400
6	400	450
7	300	400
8	350	450

Thus the enamels range in order of resistance to crazing and chipping as follows: Nos. 1, 4, 2 and 3, 6, 8, 7 and 5.

As shown, No. 1 enamel is by far the most resistant to crazing and chipping. At 500°F sample No. 1*b* crazed slightly on the side where there was a depression or flaw in the casting. Otherwise there was no very apparent crazing until the enamel had been heated to 900°F. When heated to 1000°F the enamel started to fuse and when plunged into water, only the top coat chipped off.

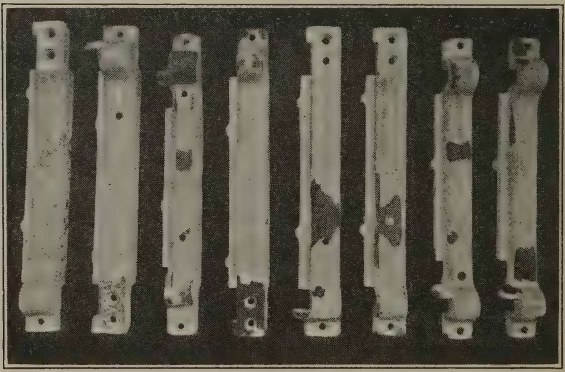

Fig. 1.

Rotating one each of the eight different samples together for five minutes in a ball mill showed that sample No. 1 is much more resistant to impact than the others. No distinction could be drawn between the other samples in this test.

Striking the samples a blow with a hammer also showed No. 1 to be the most resistant to chipping, with Nos. 2 and 3 following.

The enamel on samples Nos. 1, 2, 3 and 4, made by the wet process, did not chip completely off the iron when heated and cooled. Much of the first coat still adhered to the piece after testing. On the other hand, both coats of enamel on these samples made by the dry process chipped off together with the exception of sample No. 6 where part of the first coat still adhered to the iron. (See Fig. 1.) This was also true of the samples when

TABLE I—RESULTS OF CHIPPING AND CRAZING TEST

Temp., °F.	200°	300°	350°	400°	450°	500°	550°	600°
(1*a*)	OK	OK	OK	Small chip on edge	No change	No change	No change	No change
(1*b*)	OK	OK	OK	OK	OK	Crazed at flaw in casting	No change	No change
(2*a*)	OK	Slight crazing on the end	No change	Slight chip on edge	Badly chipped and crazed	No further test	......	......
(2*b*)	OK	OK	OK	OK	Small chip on corner	No change	Slight crazing	Corner badly chipped. Medium crazing[1]
(3*a*)	OK	Slight crazing on the end	No change	Increased crazing. Small chip on edge	Badly chipped and crazed	No further test	......	......
(3*b*)	OK	OK	OK	OK	Slight crazing	No change	Slight chipping on corner	Badly chipped. Slight crazing[1]
(4*a*)	OK	Slight chip on corner	No change	No change	No change	Badly chipped and crazed	No further test	......
(4*b*)	OK	OK	OK	OK	OK	Badly chipped. No crazing	No further test	......
(5*a*)	Slight crazing	Badly chipped and crazed	No further test	....	......	......	......	......
(5*b*)	OK	Slightly crazed	No change	No change	Increased crazing	Badly crazed	Badly chipped and crazed	No further test
(6*a*)	OK	One slight craze mark	No change	One large chip	Badly crazed and chipped	No further test	......	......
(6*b*)	OK	OK	OK	OK	Medium crazing	Badly crazed	Chipped on corner	Badly chipped[1]
(7*a*)	Slight crazing	Badly chipped and crazed	No further test	....	......	......	......	......
(7*b*)	OK	OK	OK	OK	Badly chipped and crazed	No further test	......	......
(8*a*)	Slight crazing	Medium crazing	No change	Badly crazed	Badly chipped and crazed	No further test	......	......
(8*b*)	OK	OK	OK	OK	Slightly chipped	Badly chipped	No further test	......

[1] No further test beyond 600°.

TABLE I—(*Continued*)

RESULTS OF CHIPPING AND CRAZING TEST

Temp. °F		650°	800°	900°	1000°
Sample	(1*a*)	Very slight crazing.	Cover coat slightly chipped	Slightly increased crazing	Enamel started to fuse. Only second coat chipped off.
	(1*b*)	No change	No change	do.	do.

tested by impact, all of which tends to show that enamels applied to cast iron by the wet process adhere more strongly to the iron than those enamels applied by the dry process.

Sample No. 6, where the enamel was applied thin, appeared to be a little better than sample No. 5, made at the same plant but applied thicker.

Results

All eight enamels were OK when tested at 120°F. The results of further testing are shown in Table I.

Conclusion

In general, with the enamels tested herein, those enamels applied by the wet process appear to be more resistant to crazing and chipping by sudden temperature change and perhaps to impact, than those enamels applied by the dry process.

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AVENTURINE GLAZES[1]

By C. W. Parmelee and John S. Lathrop

ABSTRACT

The aventurine is a special type of the crystalline glaze in which the separation of isolated individual crystals in the magma gives rise to the characteristic appearance of flitters or spangles suspended in a glass. The glazes may exhibit all degrees of crystallization from a few minute crystals to crowding of the magma with crystals, thus forming a matt texture, or in extreme cases a rough unsightly surface.

Iron is most commonly used for this development, although chrome, copper and uranium aventurines have been mentioned in literature.

In this investigation, we are reporting the results obtained by various students who have participated in our program of a rather extensive study of these glazes. Some of the data have been had from class exercises, other portions have been the results of investigations conducted for theses.

Scope of the Investigation

In this investigation a study has been made of the effects of variations in the alumina, ferric oxide, boric acid and RO members in a cone 1 aventurine glaze, as well as the correct heat treatment for the best development of the aventurine effect.

Method of Investigation

The investigation was divided into two parts. In the first part a good aventurine glaze maturing at cone 1 was selected, as the base, and the effects of variations in the alumina, boric acid and ferric oxide content, and the effects of different heat treatments were studied. For the second part of the investigation, the best aventurine glaze developed in the first part was used as a basis for the investigation of the effects of variations in the RO constituents of the glaze.

The general formula of the glazes under investigation with all the variables indicated was as follows:

$$\begin{array}{l} 0.0 \text{ to } 1.0\ Na_2O \\ 0.0 \text{ to } 1.0\ K_2O \\ 0.0 \text{ to } 1.0\ CaO \\ 0.0 \text{ to } 1.0\ PbO \end{array} \left\{ \begin{array}{l} 0.05 \text{ to } 0.15\ Al_2O_3 \\ 1.25 \text{ to } 2.00\ B_2O_3 \\ 0.75 \text{ to } 0.95\ Fe_2O_3 \end{array} \right\} 7.00\ SiO_2$$

For the first part of the experiment, only the R_2O_3 members were varied; the RO was kept constant at 1.0 Na_2O. The series was divided into three groups; the first group contained 0.05 moles of alumina; the second group contained 0.10 moles of alumina; and the third group contained 0.15 moles of alumina. Each group was divided into a rectangular field with four horizontal members representing variations in B_2O_3 content from 1.25 moles to 2.0 moles, and five vertical members representing variations in the Fe_2O_3 content from 0.75 moles to 0.95 moles.

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[1] Recd. April 25, 1924.

All the trials were placed in glazed saggers and were burned to cone 1 in 24 hours in a down-draft coal-fired kiln such as has been described by R. T. Stull and R. K. Hursh.[1] The results of the first burn showed considerable differences of temperature in different parts of the kiln. Cones were placed in each sagger so that the heat treatment of each trial could be noted. The next burn was conducted at cone 3 and the final burn was conducted at cone 1. In both of these burns the variations were small.

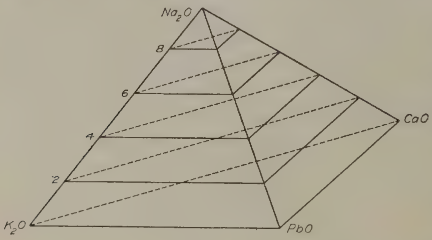

FIG. 1.

In the second part of the investigation, the variations were made in the RO members as already shown and the trials were burned to cone 1. It is difficult to picture the fields covered by the four variables. However, they may be visualized as lying in a series of planes which intersect a pyramid with a triangular base and parallel to the same. At the apex of the pyramid, 1.00 equivalent Na_2O is located and 1.00 equivalent K_2O; 1.00 equivalent CaO; and 1.00 equivalent PbO are the three corners of the base of the pyramid. A clearer conception may be had by reference to Fig. 1.

These glazes were burned to cone 1 in glazed saggers as before and the effects of the varying RO members were noted and tabulated.

Method of Preparing Glazes

For the first burn of the first part of the investigation and for the second part, all the glaze materials were fritted. For the second and third burns of the first part, 0.05 moles of alumina were omitted from the frit and added as raw clay as an aid in keeping the frit in suspension during dipping. Drop-fritting the glaze was not employed, but the charge was brought to a quiet fusion and then poured into cold water.

After quenching, the frits were ground in porcelain ball mills with water until they readily passed a 100-mesh screen. In order to keep the frits in suspension in water during grinding a strong solution of ammonia water was added.

In the first part of the investigation, the four corner frits of groups I, II and III were prepared as described and all the intermediate glazes were obtained by molar blending. This method of blending is described by Purdy and Fox in their work on fritted glazes.[2] In the second part, the four corner frits of the pyramid were prepared and the intermediate glazes were blended in the same manner as for the previous group.

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[1] "Designs of Seven Test Kilns," *Trans. Amer. Ceram. Soc.*, **16,** 431(1914).

[2] R. C. Purdy and H. B. Fox, "Fritted Glazes," *Trans. Amer. Ceram. Soc.*, **9,** 95 (1907).

Materials Used

The following potter's materials were used for making the glazes: English china clay, borax, boric acid, red lead, whiting, soda ash, potassium carbonate, ferric oxide.

Part I[1]—Trial Pieces

The trial pieces were rectangular white biscuit wall tile.

Cone 1

The variations in the formulae of all the glazes of the first part were within these limits:

$$1\ Na_2O \quad \left\{ \begin{array}{c} 0.05 \text{ to } 0.15\ Al_2O_3 \\ 1.25 \text{ to } 2.00\ B_2O_3 \\ 0.75 \text{ to } 0.95\ Fe_2O_3 \end{array} \right\} \quad 7.00\ SiO_2.$$

They were divided into three groups in which the alumina varied; that for Group I, 0.05 Al_2O_3; for Group II, 0.10 Al_2O_3; and for Group III, 0.15 Al_2O_3. In all groups 1.00 Na_2O and 7.00 SiO_2 were constant and the B_2O_3 and Fe_2O_3 varied as shown in Fig. 2.

The figures at the left and bottom indicate the moles of oxide and the letters at the top with the figures at the bottom and the group number locate the glaze as IIC4, IIIB5, etc.

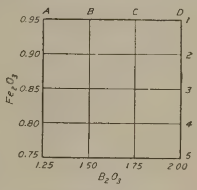

FIG. 2.

Discussion of Results

The results indicate that with these variations in glaze composition, an alumina content of 0.15 equivalent produces better conditions for the development of aventurine glazes than does a lower alumina content. Also they seem to indicate that the highest alumina content produces more easily fusible glazes than do the lower alumina contents. This accords with the findings of Purdy and Fox.[2]

With one exception the glazes with 0.05 equivalent of alumina showed no aventurine tendencies. This may be due to the heat treatment which they received, since all of these glazes were burned either too high or too low. However, some of the other glazes with a higher alumina content which were burned either excessively high or excessively low showed brighter glazes and contained aventurine spangles. The one glaze in this group showing a tendency towards the development of an aventurine effect was the one highest in boric acid and highest in iron oxide. The spangles showed only under the electric light; otherwise the glaze was dull and unsatisfactory.

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[1] An experiment conducted by students in the Department of Ceramic Engineering, University of Illinois, in the first semester of 1921-22.

[2] "Fritted Glazes," *Trans. Amer. Ceram. Soc.*, **13,** 177 (1911).

The area of high iron oxide and medium boric acid content with low alumina gave bright brown colored glazes which lost their gloss in a little while.

All of the glazes containing 0.10 equivalent of alumina were bright. In this group, only the glazes highest in iron oxide and highest in boric acid showed any spangles. In some of the glazes, these were thin, minutely divided spangles, but in one glaze the large metallic appearing separations were rather attractive, but not the aventurine. The color range does not seem to be uniform except that the glazes high in iron oxide and low in boric acid and those low in iron oxide and high in boric acid were lighter colored than the others. The other colors were dark yellow, brown, black and purple.

The group containing 0.15 equivalent of alumina showed the greatest tendency to produce aventurines. All of these glazes except the ones high in iron oxide and low in boric acid, and those high in boric acid and low in iron oxide showed more or less aventurine spangles. These exceptions produced yellow colored glazes, while the others produced darker colors. The glazes lowest in iron oxide and lowest in boric acid showed the best aventurines, producing large patches of the true goldstone effects. In this group, the glazes highest in iron oxide and highest in boric acid had a tendency to produce matt textures.

In all the groups the glazes highest in iron oxide and lowest in boric acid and those highest in boric acid and lowest in iron showed more of a tendency to craze than the others.

In each group the composition with the highest iron oxide and highest boric acid content produced a bright brownish purple colored glaze which had a good, glossy finish and good texture. This color grew darker as the alumina content increased. The glaze of this composition in the 0.15 alumina group had the best color and finish, and was glossy and smooth without pinholes or crazing. It was uniform in color and texture and was crowded thickly with very minute aventurine spangles which showed best under the electric light. The glaze developed well even to the very edges of the piece. It matured at cone 05 as a very pleasing glaze.

Conclusions

1. 0.15 equivalent of alumina gives a better condition for the development of aventurines than a lower content.

2. Low iron oxide together with a low boric acid content in this glaze with highest alumina content produces the best goldstone effects.

3. High iron oxide content with high boric acid in the high alumina glaze tends to give matt textures.

4. High iron oxide with low boric acid and high boric acid with low iron gives yellow glazes with crazing tendencies.

5. The best temperature to develop these aventurines is cone 1 or cone 2.

6. A good bright, brownish purple glaze maturing at cone 05 is developed with 0.15 alumina, 0.95 iron oxide and 2.00 boric acid in this base glaze.

Cone 3 (1190°C) Burn

The glazes used in this series were the same as those used for the first burn except that 0.05 moles of alumina were left out of the frit and added to the mill batch as raw clay in order to aid in holding the frit in suspension.

The glazes were burned to cone 3 in glazed saggers in the same kiln as used before.

Discussion of Results of Cone 3 Burn

The correctness of the conclusions drawn from the first burn was confirmed. Evidently cone 3 is too high a temperature for these glazes, as the results were better at a lower cone. One point brought out quite strongly by this burn was the effect of alumina on the development of aventurine crystals. The glazes in Group I with only 0.05 moles of alumina were nearly all entirely crystallized, indicating that the glaze was quite fluid at cone 3, thus facilitating crystal separations. The glazes in Group III, on the other hand, did not crystallize so freely, indicating that the glazes in this group were more viscous at cone 3. The glazes of Group II were intermediate in this respect.

The tendency of the Al_2O_3 seems to give a deeper and richer color to the glaze as the quantity increases as well as to decrease the fluidity of the glaze.

The glazes with lowest iron and lowest boric acid content seem to give the best aventurine crystals.

Conclusions from Cone 3 Burn

1. Cone 3 is too high a temperature for these glazes.

2. Low boric acid and low iron content give the best aventurine crystals.

3. The other conclusions of the first burn were verified.

Third Burn of First Part. Cone 1

This series was the same as the second series but was burned at cone 1 with careful heat regulation and the kiln was held a little longer time at the maximum temperature.

Discussion of Results of the Third Burn

As in the previous burns, the higher alumina content apparently gives a more viscous glaze and retards crystallization to a very marked degree. Cone 1 is evidently the proper maturing temperature for these glazes since most of them matured glossy and smooth.

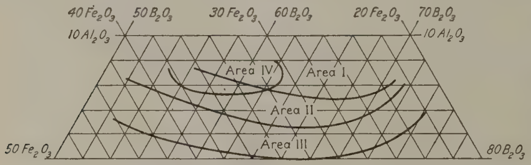

FIG. 3.—Showing areas of best aventurine glazes.

I	Area of	Least gloss
II		Aventurines
III		Most gloss
IV		Best Aventurines

The low iron and low boric acid glazes give the best aventurines and the most beautiful glazes. Increased iron content seems to give the glaze a more reddish color than the lower iron content. Such glazes as do not develop any aventurines nevertheless produce beautiful mottled purple colors.

Conclusions from the Third Burn

The results of this burn confirm the conclusions drawn from the two previous burns.

General Conclusions on Effect of Heat Treatment and Variations in the Content of Alumina, Iron Oxide and Boric Acid

1. The compositions studied yield aventurine glazes which are best developed at cone 1.
2. Increasing the alumina content retards the development of the aventurine.
3. The best aventurine glazes were obtained with low iron and low boric acid content.
4. The least crazing was found in areas of maximum crystallization.
5. In areas where no crystallization takes place, beautiful mottled, reddish purple glossy glazes were produced.

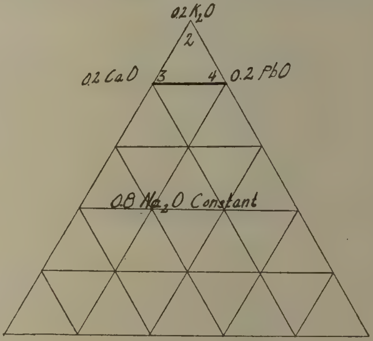

FIG. 4.

6. To produce the best results, the glaze materials must be fritted together before being applied to the piece.
7. Careful firing and cooling is necessary for the proper development of aventurine glazes.
8. The best aventurine glaze produced had the following composition:

$$1.00\ Na_2O \left\{ \begin{matrix} 0.15\ Al_2O_3 \\ 1.25\ B_2O_3 \\ 0.75\ Fe_2O_3 \end{matrix} \right\} 7.0\ SiO_2$$

When the molar equivalents of alumina, boric acid and ferric oxide are plotted as percentages of molar equivalents the results may be shown as in Fig. 3.

Part II

In the second part of the investigation[1] an attempt was made to determine the effects of variations in the RO group on the development of aventurine glazes and their maturing temperature. This was accomplished as outlined in the "Method of Investigation" (see p. 567). The triaxial diagrams showing the RO compositions of each glaze are given in Figs. 4, 5, 6, 7, and 8.

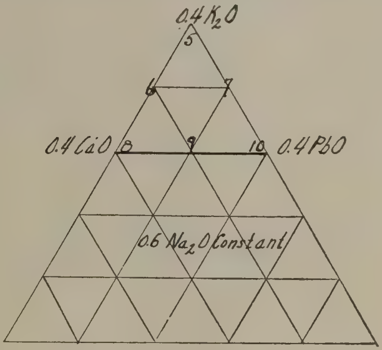

FIG. 5.

The method of preparing the glazes and of blending is the same as given for Part I, Series I and they were fired at cone 1.

The general glaze formula with the RO variations used in this part was as follows:

$$\begin{array}{l}0.0 \text{ to } 1.00\ Na_2O\\ 0.0 \text{ to } 1.00\ K_2O\\ 0.0 \text{ to } 1.00\ CaO\\ 0.0 \text{ to } 1.00\ PbO\end{array}\left\{\begin{array}{l}0.15\ Al_2O_3\\ 1.25\ B_2O_3\\ 0.75\ Fe_2O_3\end{array}\right\}\ 7.0\ SiO_2$$

Discussion of Results of Glost Burn with Variable RO

Soda seems to be the member of the RO group which most assists crystallization. The glazes centered around the soda vertex of the pyramid all showed a marked development of aventurine and the amount diminished toward the other vertices. Potash was the next agent most conducive to this formation. Lime and lead both seem to hinder the formation of crystals, probably because of the higher viscosity of the glazes containing these RO members.

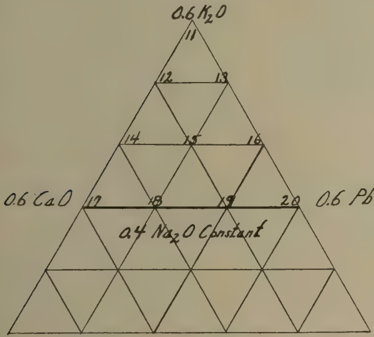

FIG. 6.

Lead and lime alone both made the glazes more refractory so that their best maturing temperature is above cone 1. Lime made the most refractory glaze of all.

The only effect upon the color noted was a reddish purple tinge which became more pronounced as the lead vertex was approached, becoming quite red-purple. From the above work, the following conclusions are deduced:

---

[1] Results obtained by John S. Lathrop in a thesis prepared for partial fulfilment of the requirements for the degree of B.S. in Ceramic Engineering.

1. Soda more than any of the other RO members employed aids in the production of aventurine glazes. A little soda makes a great difference in promoting the formation of aventurine.

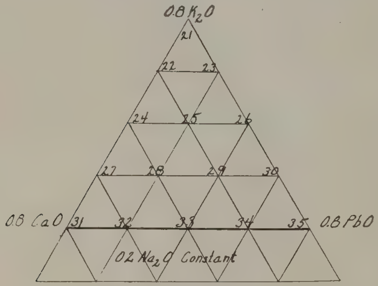

FIG. 7.

2. Potash is the second best agent in the production of aventurine glazes and lead is next.

3. Lime has a marked influence in promoting refractoriness of the glaze.

4. The color of the glazes is little affected by the RO members employed excepting lead which develops a decidedly reddish purple color.

General Conclusions

1. An increase in the iron content increases the size and the number of crystals and also the refractoriness of the glaze.

2. An increase of Na_2O increases crystallization.

3. Aventurines were not present when the CaO was increased to 0.4 equivalent.

4. Decreasing the lead and increasing soda increases crystallization and decreases the gloss.

5. A low iron oxide content (0.75 moles) together with a low boric acid content (1.25 moles) with high alumina (0.15 moles) and silica (7.00 moles) content produce the best goldstone effect.

6. Crazing occurs least in the areas of best crystallization. This is contrary to the behavior of most crystalline glazes, but seems consistently true with aventurines.

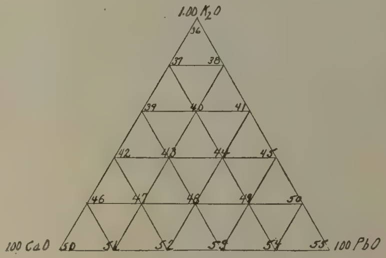

FIG. 8.

7. The order of beneficial effect upon crystallization of the RO members studied is as follows: 1. Soda; 2. Potash; 3. Lead; 4. Lime.

8. The best results were obtained with a medium thick application of the glaze, *i. e.*, not over 2 mm.

Bromberg[1] in his investigation of another field of aventurines in which the bases were soda, potash and lead, and the silica, ferric oxide and boric acid were in lesser amounts than used by us, obtained results which are in accord with conclusions Nos. 2, 4, and 7. He obtained aventurines when the CaO was increased to 0.4 equivalent while we were unable to produce them with that amount present.

UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

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[1] Thesis, Univ. of Illinois, 1915

THE METHOD OF SELECTING REFRACTORIES FOR MARINE PURPOSES OF THE NAVY[1]

By H. H. Norton[2] and R. L. Porter[3]

ABSTRACT

Trouble was experienced with refractories when oil fuel supplanted coal in the furnaces of naval boilers.

The selection of refractories for naval oil-fired boiler furnaces done at the Philadelphia Navy Yard is described.

The Navy's test for refractories (chemical analysis, fusion point determination, and the Simulative Service Test). The Simulative Service Test.—Description of, and its value in obtaining satisfactory refractories. The Navy's "Acceptable List of Refractories." The results of the Simulative Service Test (about 26% of the refractories submitted passed).

About fifteen years ago when the Navy began to burn oil fuel in place of coal in boiler furnaces on shipboard, it found that brands of fire brick which had previously given good service were no longer satisfactory. Some melted, others shrank, still others spalled.

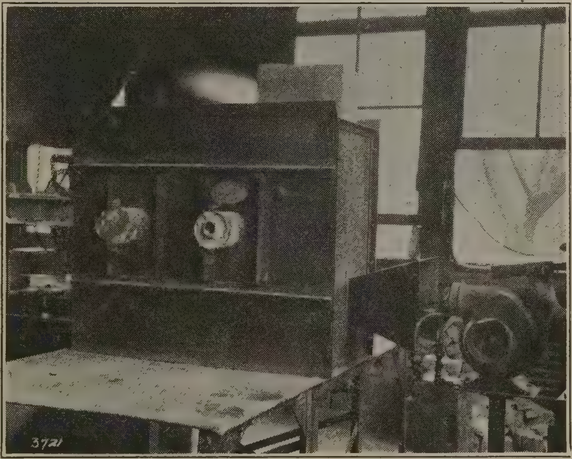

Fig. 1.—Refractory test furnace in operation.

With oil fuel higher temperatures could be obtained; then, too, temperature changes were more rapid due to the sudden lighting and extinguishing of burners. A ship being brought to anchor within a few moments of the completion of a full-power trial would naturally have extreme temperature changes in the brickwork of its furnaces. Here the condition would in some cases represent a boiler being suddenly cut out after operating at a 500% rating. Again, the Naval type express boiler may, in emergency, be required in thirty minutes to have a full head of steam from a dead condition, or the ship capable of full power with but short notice.

On the other hand, the brickwork with fuel oil did not have to withstand the attacks of the slice bar or slagging, as did the refractories in a coal-burning boiler.

---

[1] Presented by Mr. Porter at the Atlantic City Meeting, Feb., 1924 (Refractories Division).

[2] Lieut.-Comdr., U. S. N.

[3] Lieut., U. S. N.

Prior to the advent of oil fuel, a fire brick was considered satisfactory if it withstood a temperature of 2800°F for three hours followed by an immersion in water at 80°F. After the adoption of oil fuel, it became necessary to frame appropriate specifications and provide adequate tests for the refractories which were to be used in the furnaces of Naval boilers.

In 1912 the Philadelphia Navy Yard, having been assigned the task of testing refractories, installed a small electric furnace somewhat similar to one developed at the Bureau of Standards for determining fusion points. Records were kept of the fusion points and also of the chemical analysis of each of the refractories examined, and in 1916, from this data, Navy specifications were issued. These specifications required, in part, that fire brick and fire clay have an analysis of approximately 54% silica, and 41% alumina with a maximum of 5% fluxes. 3100°F was set as the minimum fusion point for fire brick; fire clay was required to have a fusion point of 3000°F or over.

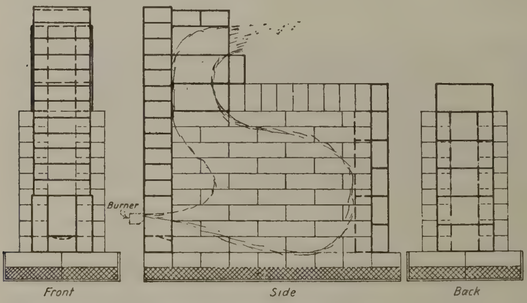

Fig. 1*a*.—Refractory test furnace with side insulation and sheet metal casing removed.

Some time later, when a brand of fire brick, which met these requirements, failed in a boiler, it became apparent that the specifications did not eliminate all bricks which were unsatisfactory for use in Naval oil-fired boiler furnaces. Then, lining boiler furnaces of the refractories to be tested was resorted to at the Fuel Oil Testing Plant. However, such lining was not only slow and expensive, but also frequently interfered seriously with tests of oil-burning equipments being conducted on the same boiler, and some other means for obtaining conclusive results was recognized as being desirable.

A Simulative Furnace Test

In 1918 a small oil-burning furnace was constructed at the Fuel Oil Testing Plant for testing insulating materials. The furnace consisted merely of a sheet metal casing, 19″ x 24$^{1}/_{2}$″ x 36″ inside dimensions, which surrounded a brick box. A 3″ space between the brick and the casing held the insulation under test. A modification of this furnace was then developed for the purpose of testing fire brick, and the test was known as the Simulative Service Test.

The Simulative Service Test is conducted in a small oil-fired test furnace. One side-wall is constructed of fire brick and fire clay of a brand which has given satisfaction in service. The other side-wall is built of the brand of fire brick and fire clay under test. Each side-wall consists of nine rows of 9″-straight bricks laid with the 9 x 2.5 inch faces to the flame. Each row is 3.5 bricks in length. The thickness of each of the walls is the width of one brick, *viz.*, 4.5 inches. The distance between the competing side-walls is only 4.5 inches, which insures both walls being subjected to the same treatment. Both walls are uniformly backed with 3 inches of the same insulation. An air-atomizing fuel oil burner is used. The flame sweeps the length of the furnace, curves upward, returns to the front and then leaves the furnace.

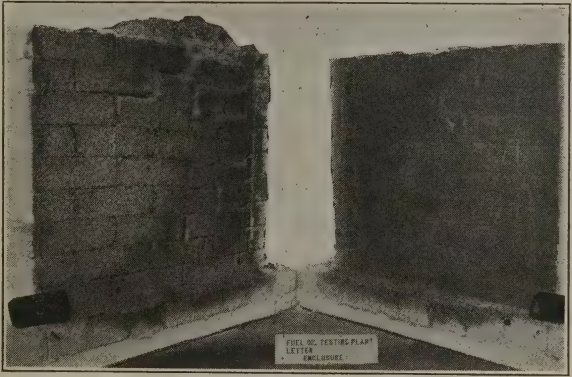

Fig. 2.—Standard wall (on right) in very good condition. Test wall (on left) shows shrinkage and deformation at rear.

The test, until a recent date, consisted of three "runs," each of 24 hours duration, at furnace temperatures of 2800°F, 2900°F and 3000°F, respectively. Recently, looking to the future, the 2800°F "run" has been eliminated and a product which, at the end of a 3000° F "run," shows possibilities of withstanding a "run" at 3100°F is subjected to same. If successful, it is given special classification. This latter "run," however, has no bearing on recommendations submitted as regards present requirements.

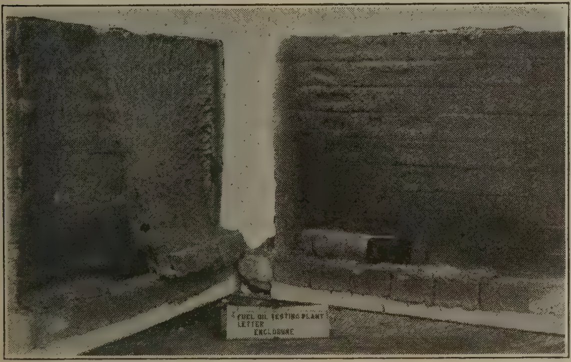

Fig. 3.—Standard wall (on right) in good condition. Test wall (on left) shows considerable fusion at rear.

During each "run," furnace temperatures are determined at quarter-hourly intervals by sighting into the furnace over the burner, with an optical pyrometer.

Temperatures at the front and rear of the outer face of the brickwork of each side-wall are determined at half-hourly intervals, with an optical pyrometer, sighting on the brickwork through alundum tubes, the ends of which are placed flush with the wall. The tubes are carefully lagged and plugged to reduce the radiation losses to a minimum.

A spalling test is conducted at the conclusion of each "run" by injecting cold air at high velocity into the furnace immediately after shutting off the oil supply to the burner. The injection is continued until the walls are cool.

The comparative heat-insulating properties, together with the relative conditions of the side-walls, determine whether or not the material under test is acceptable for use in the Naval service.

The test demonstrates conclusively the capacity of the refractories under examination to withstand satisfactorily the conditions to which they are subjected in the furnaces of naval oil-fired boilers. Brands which have given satisfaction in oil-fired boilers on shipboard have passed the test in good condition. On the other hand, fire brick and fire clay, which pass the test, perform satisfactorily in service.

The Navy's Acceptable List

The Navy maintains what is termed an acceptable list, which consists of those fire bricks (by trade name) which have met the prescribed requirements for fusion point and chemical analysis and have passed the Simulative Service Test. Manufacturers having brands on this list are requested to bid upon Navy contracts. A manufacturer, who does not have a brand of refractory upon the acceptable list, but who desires to sell his product to the Navy, submits a request for test to the Navy Department (Bureau of Engineering). The Fuel Oil Testing Plant at the Philadelphia Navy Yard is then directed to make the necessary arrangements for the tests. The manufacturer submits several bricks and a few pounds of clay for chemical analysis and fusion point determination and, if the materials come within the limits of Navy specifications, he is requested to submit additional sam-

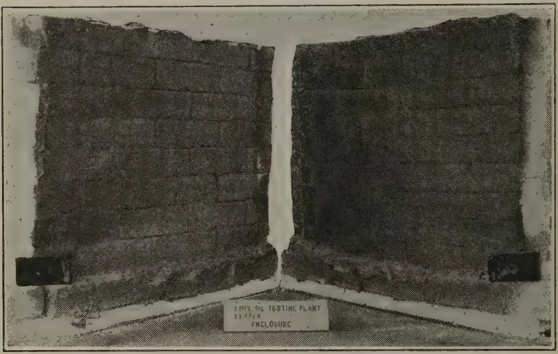

Fig. 4.—Standard wall (on right) in good condition. Test wall (on left) shows cracking.

ples to undergo the Simulative Service Test. Should his product pass the test, its name is listed with the acceptable refractories and he is permitted to bid on Navy contracts. Should he be the successful bidder, his brand is generally used during the ensuing year as the standard wall in the test furnaces for comparison with other materials under test. Should the quality of his product deteriorate appreciably, it is found out in a comparatively short time.

The above procedure, together with the size of the present schedule for contract upon which a manufacturer is expected to bid, may be somewhat discouraging from his point of view, and he may think the Navy a bit arbitrary in its requirements. However, it should be realized that, by this method, the Navy is successful in obtaining refractories which meet its needs, and which give satisfaction in the furnaces of marine oil-fired boilers. With such results is it not probable that before long other consumers may be requiring tests for refractories which simulate their actual conditions, rather than some of the test methods at present being used?

About 27% of the refractories submitted to the Fuel Oil Testing Plant have passed the Simulative Service Test. Some were not given the Simulative Service Test because of low fusion points, as determined by pyrometric cones, or because high silica or high flux contents indicated that the Simulative Service Test was not warranted. More complete figures are given in the following table:

	No. brands submitted for test	No. brands given Simulative Service test	No. brands which passed Simulative Service Test	Percentage of those submitted which passed Simulative Service Test
Fire bricks	95	81	28	29%
H. T. cements	33	12	8	24
Plastic fire-brick materials	26	24	7	27

Considering 17 brands of fire brick that passed the Simulative Service Test with flying colors, it may be of interest to note that the average fusion point was 3175°F (about cone 31), the maximum fusion point was 3250°F (about cone 33), and the minimum 3100°F (about cone 29). At this point it may be desirable to state that, in a check determination made with Mellon Institute, the difference was one cone, the Philadelphia Navy Yard obtaining the lower result.

These 17 brands, in general, varied in color from a light cream to a light buff. Approximately 50% of the bricks contained medium-sized grog particles, 25% showed grog particles somewhat larger than medium, and about 25% possessed grog particles somewhat smaller than medium size.

The chemical analyses of the same 17 brands averaged about 51%

silica, 42% alumina, 2.5% titania and 4.5% fluxes. The silica content varied from 60% to 39%. The average weight for a *perfect* 9″-straight brick was 7.53 pounds, the maximum weight was 8.15 pounds and the minimum weight was 7.02 pounds.

Of the brands of fire brick which did not pass the Simulative Service Test, about 70% failed because of melting, about 25% because of shrinkage and cracking, and the other 5% because of a combination of reasons. No brick with an analysis of over 61% silica has survived the Simulative Service Test so far. Light-weight bricks and bricks having extremely fine- or coarse-grained cross-sections are seldom satisfactory.

Three small furnaces are operated consecutively at the Fuel Oil Testing Plant. The testing of refractories goes on night and day and a manufacturer who desires to witness the test of his product is always welcome.

FUEL OIL SECTION PLANT, NAVY YARD
PHILADELPHIA, PA.

Discussion

CHAIRMAN HARVEY: This Simulative Service Test has been embodied in the new tentative specifications adopted by the Federal Specifications Board so that for manufacturers of refractories it becomes of vital importance. In all probability these specifications will be adopted by private concerns so that it has still greater bearing.

MR. GELLER: How long has this data been available?

MR. PORTER: We compiled the data about a week ago.

MR. GELLER: At the time those specifications were written the representatives from the Navy who were present insisted that the fusion point of material which was to be subjected to a simulative test or which had any chance at all of being used by the Navy would have to have a softening cone point of 32.

MR. HARVEY: The Navy Department apparently has come down on their requirements on the fusion point. I do not think they have come down but have properly interpreted previous results. I know of one case where cone 35 was reported on a brick with which I happen to be familiar, and other laboratories were reporting cone $32^1/_2$ on the same brick.

MR. PORTER:[1] The old scale of fusion point of Seger cones was used in reporting. That is, if a brick was reported as having a fusion point of 3000°F, its fusion point was cone 26.

In 1916, the Navy Specifications for refractories required that fire brick have a minimum fusion point of 3100°F, and fire clay have a minimum fusion point of 3000°F. These fusion points were determined by Orton cones and the conversion table used was in part as follows:

---

[1] Recd. April, 1924.

Cone	°F	Cone	°F
26	3002	31	3182
27	3038	32	3218
28	3074	33	3254
29	3110	34	3290
30	3146	35	3326

Therefore, the actual requirements were that the minimum fusion points for fire brick and fire clay were about cones 29 and 26, respectively.

In reporting fusion point determinations, the temperatures corresponding to the various cones given by the above scale were used. It is our intention, however, upon the issue of new specifications by the Navy Department, to utilize the new table given below, which has recently been determined by the Bureau of Standards to be more accurate. To avoid confusion with data already at hand, both cone number and temperature in °F will be used in every report:

Cone	°F	Cone	°F
26	2822	31	3002
27	2858	32	3038
28	2894	33	3074
29	2930	34	3110
30	2966	35	3146

MR. DORNBACH: Are the results of the Navy Yard test public?

MR. PORTER: No. The report as to whether or not a brick is satisfactory is made only to the exhibitor. The reports of the tests are kept on file at the Navy Department. (Bureau of Engineers.)

MR. BALES: Have you found any brick that gave better results in the test than your standard?

MR. PORTER: We have used various brick for the standards. Any brick that is on the approved list is used as a standard. As a rule, of course, that is a brick that is being supplied under contract.

MR. BALES: If you make a fusion point determination first and if it comes below cone 31, do you not make the Simulative Service Test?

MR. PORTER: If the fusion point is below 3100°F old scale, which corresponds to about cone 29, we reject the brick without subjecting it to the Simulative Service Test.

MR. BALES: Do you change the test in any way at all if it is to be used for the coal fired boilers?

MR. PORTER: Practically all our boilers are now oil-fired. We have very few coal burning vessels. We make no tests for bricks used in coal fired boilers.

MR. BOOZE: Do you find that your marine boilers are actually being operated at temperatures as high as 3000°F?

MR. PORTER: In our boilers our temperatures fluctuate. The maximum temperature which we have obtained in the boilers was about 3050°, that at the fuel oil testing plant where the conditions are more or less ideal.

MR. BOOZE: It should be pointed out that the refractories used in these boiler settings must be capable of withstanding the punishment inflicted by operation at very high ratings with extreme temperatures. It would be a mistake to use a test identical with this one for refractories to be used in stoker fired boilers since in the latter the temperatures are, as a rule, not over 2800°F.

MR. PORTER: This is a test by which we obtain refractories that give satisfaction for our own particular use. We do not claim anything else for it.

A MEMBER: Mr. Booze's remarks are true as far as modern boiler plant practice is concerned, where they are burning coal on stokers, but where pulverized fuel is used the temperatures approach those in oil-fired furnaces, for in order to reach the high efficiency claimed for powdered fuel it is necessary to cut down the amount of excess air and naturally the flame temperature will go up and the refractory will be subjected to very high temperatures. It is common practice in some plants burning pulverized fuel to raise the temperature by cutting down the air until the walls will not run, just to the point where the slag will not run on them. So in pulverized fuel burning plants they will approach temperatures nearer those you are using in oil burning furnaces. A simulative test burning pulverized fuel would come nearer those temperatures.

ERRATA

W. E. S. Turner, "The Use of Boric Oxide in Glass Making," *Jour. Amer. Ceram. Soc.*, **7** [5], 316, last line: "maximum corrosion" should read "minimum corrosion."

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ORIGINAL PAPERS

NOTES ON THE BEHAVIOR OF REFRACTORIES IN GLASS MELTING FURNACES[1]

By Herbert Insley

ABSTRACT

Microscopic examination of used glass house refractories gives evidence about the transformations that have taken place during use, and the relative solubilities of constituents of the refractories in the glass. On this evidence it is concluded that high alumina refractories would resist the solvent action of the glass and the fluxing action of the soda in the furnace atmosphere better than fire clay refractories. Investigations are needed to find a new refractory mortar for use between silica and clay refractories in glass tanks.

A knowledge of the comparative value of different types of refractories for glass melting furnaces would be of great value to the glass manufacturers, because the life of such furnaces depends largely on the behavior of the refractories. Unfortunately, there is little, if any, available information along this line, especially where actual conditions of operation can be stated. Something, however, may be learned about the causes of failure of glass furnace refractories by macroscopic and microscopic examination of such refractories after service in a melting furnace.

It is the purpose of this paper to give the results of such examinations, to present such conclusions as may be drawn regarding the causes of failure and to suggest methods for prolonging the life of refractories.

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[1] Published by permission of the Director of the Bureau of Standards of the U. S. Department of Commerce. Recd. May 15, 1924.

The usual glass melting furnace refractories are silica brick and clay blocks. The silica refractories are used in the crowns and upper side walls of tanks where they are exposed to the action of the dusts and gases in the furnace atmosphere, but not to the direct solvent action of the molten glass, while the clay refractories are used in the lower side walls and bottoms of tanks and pots, where they are subjected to such a solvent action. Clay refractories are also used to a limited extent in positions where they are exposed to the furnace atmosphere.

The composition and physical properties of the molten glass are, of course, factors affecting the behavior of the refractory walls. Most of the examinations reported in this paper were made on refractory materials used in melting the soda lime glasses.

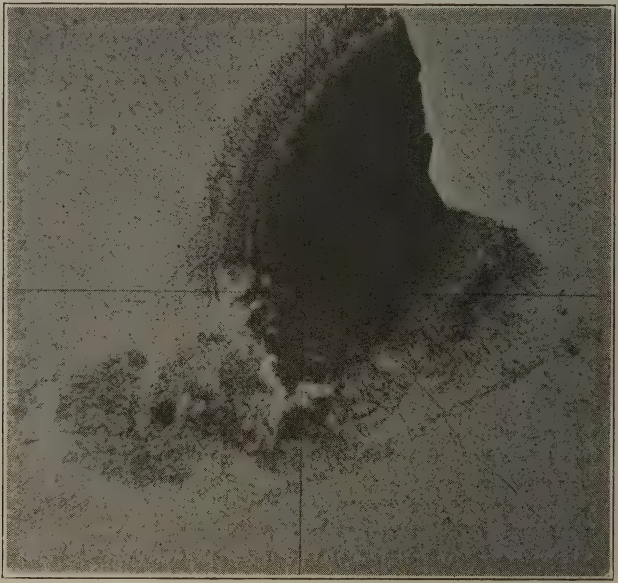

FIG. 1.—Photomicrograph of clay stone in glass, showing area of clay (dark gray), surrounded by a narrow zone of corundum crystals which in turn is surrounded by a broader zone of nephelite crystals. Ordinary light. Magnification 75 ×.

During the manufacture of the clay refractories reactions take place which are now fairly well understood. After the free water and water of crystallization have been driven off, the clay minerals (minerals of the kaolinite type) undergo some sort of decomposition; either into Al_2O_3 and SiO_2 or into different combinations of the two. At still higher temperatures recombination of these constituents takes place and a crystalline compound in a glass matrix is formed. The crystalline compound was formerly thought to be sillimanite ($Al_2O_3.SiO_2$) but recently Bowen[1] has adduced evidence to show that the compound actually appears to be $3Al_2O_3.2SiO_2$. This question cannot be finally decided until more data have been obtained but in this paper the compound will be called $3Al_2O_3.2SiO_2$. Clays burned to a high temperature consist essentially of this crystalline compound, and a glass matrix composed of the alkalies, alumina and silica.

Clay Refractories below the Glass Line

Clay refractories below the glass line of the pot or tank and in contact with the glass are subjected to high temperatures and to the solvent action of the glass. The narrow white zone so often seen at the contact of refractory and glass is composed of a net-work of needle-like crystals of $3Al_2O_3.2SiO_2$ in a matrix of glass. Farther within the refractory the crystals are small and poorly developed and amorphous materials still remain in the body. The glassy matrix of the white layer seems to dissolve readily in the molten soda-lime glass and the surfaces of the $3Al_2O_3.2SiO_2$ crystals also show traces of corrosion and solution.

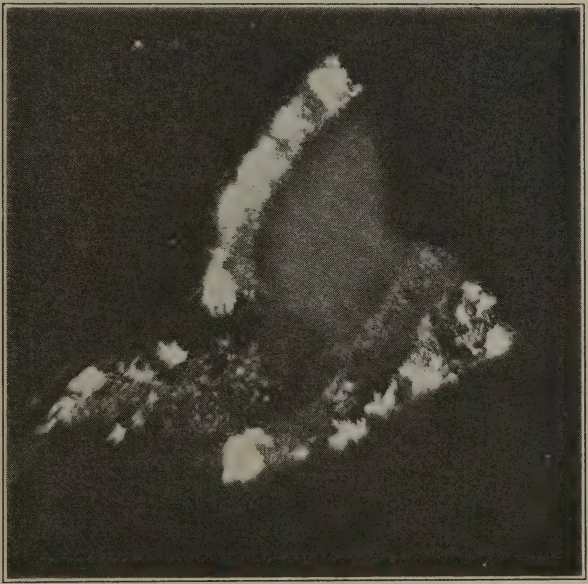

FIG. 2.—Same as Fig. 1 but with crossed nicols. The area of clay which is in part transformed to $3Al_2O_3.2SiO_2$ and glass appears dark gray in photograph. The corundum crystals are seen as fine bright needles and points of light, while the nephelite forms a light, cloudy zone. Magnification 55 ×.

Adjacent to the contact zone but within the soda-lime glass there is very frequently a layer of small, hexagonal plates of corundum (Al_2O_3) (Figs. 1 and 2). In a previous paper[2] corundum crystals of this character were said to be caused by the loss of water and recrystallization of gibbsite, $Al(OH)_3$ or diaspore, $AlO(OH)$, in the refractory. Further study indicates, however, that crystals of corundum are formed by the action of glass on clay refractories containing no aluminum hydroxides originally. It now seems probable that as the aluminum silicates dissolve in the molten glass the concentration of alumina in the contact zone increases until the solution is super-saturated with respect to alumina and corundum is deposited simultaneously with the further solution of the clay.

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[1] "The System Al_2O_3–SiO_2," N. L. Bowen and J. W. Grieg, *Jour. Amer. Ceram. Soc.*, **7** [4], 238 (1924).

[2] Insley, "A Study of the Origin and Cause of Stones in Glass," *Jour. Amer. Ceram. Soc.*, **6** [6], 715(1923).

Figs. 3 and 4, show a thin section of a grog particle of a clay block in contact with a soda-lime glass. The grog particle itself has been largely converted to needle-like crystals of $3Al_2O_3.2SiO_2$ and glass, the crystals being so small and intermeshed that they are not distinguishable in the photograph. At the contact of grog particle and glass a zone of thin hexagonal plates of corundum has been formed. The plates appear as needles (plates turned on edge) in the photograph. Next to the zone of corundum and farther from the refractory is a zone of nephelite ($Na_2O.$-$Al_2O.2SiO_2$), the crystals of this compound usually occurring as indistinct

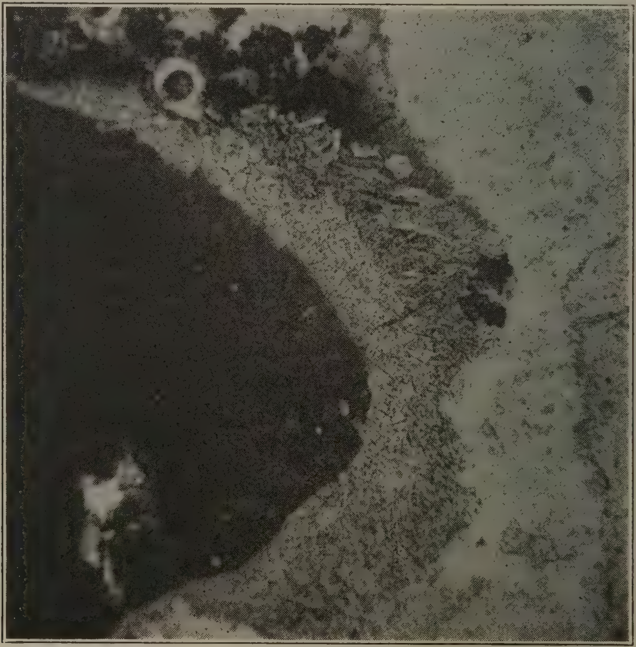

Fig. 3.—Contact of a grog grain in the clay wall of a tank with the glass. The corundum crystals in the zone next to the grog grain appear as needles and small rounded grains. The zone next to the glass is full of skeleton crystals of nephelite. Ordinary light. Magnification 80 ×.

skeleton crystals which contain considerable glass as inclusions. It is probable that the nephelite crystallizes during the cooling of the melt. The zone of nephelite is rather infrequently observed and the zone of corundum is by no means a characteristic of every contact between clay refractory and glass. Where the flow of glass past the refractory wall is rapid the corundum is probably soon swept away or dissolved in the unsaturated solution, and if the clay refractories are high in silica the corundum may never form.

The reactions which take place at the contact of refractories and glass give some indications of the relative solubilities of silica, $3Al_2O_3.2SiO_2$ and corundum in the glass. The glass which forms the matrix in clay refractories burned at high temperatures contains a high percentage of silica. It dissolves readily in the molten soda-lime glass leaving behind the mesh-work of crystals of $3Al_2O_3.2SiO_2$. These crystals are frequently found floating unattached in the glass close to the contact with the refractory. The rounded ends and corroded surfaces of the crystals and their disappearance in the glass away from the glass-refractory contact are evidence that they dissolve, although more slowly than the matrix in which they were originally embedded. The fact that corundum crystallizes after $3Al_2O_3.2SiO_2$ has been dissolved by the soda-lime glass indicates that corundum is much less soluble in the glass than the $3Al_2O_3.2SiO_2$.

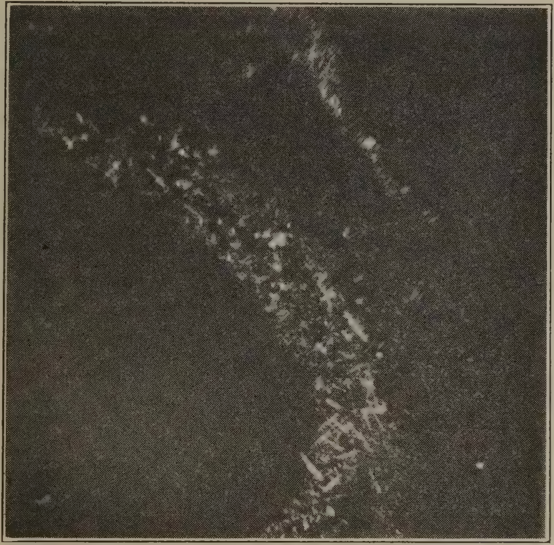

Fig. 4.—Same as Fig. 3 but with crossed nicols. The corundum crystals form a band of bright needles and points. Magnification 80 ×.

The relative insolubility of corundum as compared with the aluminum silicate and the silicates of alumina and the alkalies suggests that a high alumina refractory for the lower side walls and bottom blocks of tanks melting the soda-lime glasses would offer greater resistance than clay refractories to the action of the glass. A factor that must be considered in the development of a high alumina refractory is the relative compositions of the grog and the bond. The usual alumina refractories are composed of grog particles with a high percentage of alumina bonded with a clay or other material that is lower in alumina and higher in silica. When material of this nature is exposed to the action of the molten glass it is likely that the bond will be dissolved readily leaving the grog to form troublesome and almost insoluble stones in the glass. It is essential then, that both grog and bond have approximately the same composition, especially with regard to silica and alumina.

Refractories above the Glass Line

Refractories above the glass line are exposed to the action of gases or dusts in the furnace atmosphere, the most important of which are sodium compounds. These may be present either as gases, or as sodium carbonate or sodium sulphate in the dusts from the unmelted batch materials. They undoubtedly have a decided fluxing action on refractory blocks whose surfaces are exposed.

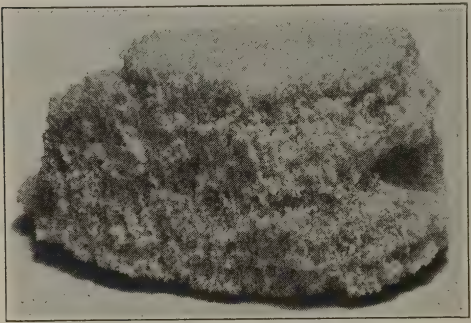

FIG. 5.—Incrustation on the surface of silica brick in the upper walls of a glass tank. The upper surface is the contact between silica brick and incrustation.

Silica brick which have been used in the crown and side walls of tanks have a vitreous luster on their exposed surfaces and under the microscope are seen to contain considerable glassy material. Evidently the soda forms a compound with the silica which is liquid at furnace temperatures. The liquid is either so viscous or so small in amount that it does not readily drip away from the brick for silica brick which have been in service for long periods have not been corroded to any great extent.

An incrustation observed on the surfaces of silica brick used in the side walls of a tank melting bottle glass is of interest in this connection. The incrustation was a white, coral-like material the appearance of which is well seen in Fig. 5. It covered the surfaces of the silica brick in the upper side walls between the regenerator ports and reached its maximum thickness of four inches between the third and fourth and between the fourth and fifth ports from the filling end on both sides of the tank. This was probably the hottest cross-section of the tank. The incrustation extended as far as the first regenerator port from the filling end and as far as the bridge wall toward the drawing end. It was easily broken away from the surface of the silica brick and the brick itself showed very little evidence of corrosion. A petrographic examination of the material gave the following results: The end of the brick next to the incrustation was composed almost wholly of very small tridymite (SiO_2) crystals. The material at the contact had a vitreous appearance and was composed of glass and large tridymite crystals while farther within the incrustation itself the tridymite crystals were larger but the quantity of glass was less. Two analyses gave the following:

	a	*b*
SiO_2	91.05	94.70
R_2O_3	1.85	0.47
CaO	1.90	0.97
Na_2O	4.59	4.00
	99.39	100.14

a. Vitreous material at the contact of silica brick and incrustation.
b. Outer part of incrustation.

Apparently the soda combined with the silica to form a liquid sodium silicate which acted as a crystallizing medium for the tridymite. The constant growth of the new large tridymite crystals forced the previously formed crystals away from the face of the brick. The R_2O_3 and CaO are probably original constituents of the silica brick.

Clay refractories exposed to the gases and dusts in the furnace atmosphere are much more affected than silica refractories. On examining the interior of a bottle glass tank which had been in use about fifteen months it was found that the face of the clay blocks which were used to form the regenerator ports and the arches for the flow troughs had in all cases receded one or two inches when compared with the face of the silica brick which adjoined them.

In the melting end of the tank the effect upon the clay refractories always corresponds closely to that noted by Wilson[1] and the writer.[2] The soda combines with the alumina and silica of the clay refractories to form a liquid at furnace temperatures. Wilson found that this liquid (represented by a glass when cool) had a molecular composition of about $Na_2O.Al_2O_3.5SiO_2$. Any excess of alumina over the amount required to form a liquid of this approximate composition will crystallize as corundum. If there is an excess of both silica and alumina, then $3Al_2O_3.2SiO_2$ and either silica (tridymite or cristobalite) or corundum will crystallize, depending upon the molecular ratios of the excess silica and alumina.[3] In most of the cases studied corundum only has crystallized.

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[1] *Jour. Soc. Glass Tech.*, **2**, 197–213 (1918).

[2] *Jour. Amer. Ceram. Soc.*, **6** [6], 714 (1923).

[3] Morozewicz, *Min. Pet. Mitt.*, **18**, 22–83 (1893); also *Zeitsch. Kryst. Min.*, **24**, 281 (1895).

Figure 6 shows the typical structure in clay refractories above the glass line in the melting end of tanks. The interior of the brick is composed of $3Al_2O_3.2SiO_2$ and glass, the size of the crystals being dependent to some extent on the distance from the exposed surface. Nearer the exposed surface the percentage of aluminum silicate crystals decreases and the percentage of glass increases. Still nearer the crystalline aluminum silicate disappears and corundum appears. The surface of the refractory is covered with a crust of thin hexagonal plates of corundum, the sodium aluminum silicate having drained away. The corundum is almost invariably colored brown, probably due to the presence of iron oxide either as inclusions or as solid solution. Where the face of the block has been in contact with silica brick, the corundum often does not form, only the sodium aluminum silicate glass being present on the surface.

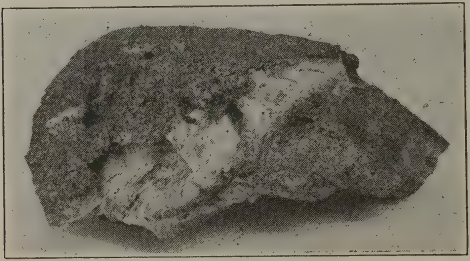

FIG. 6.—Piece of a refractory clay block which has been exposed to the gases and dust in the atmosphere of a glass tank. The dark-colored material in the lower part of the photograph is clay, partly altered to $3Al_2O_3.2SiO_2$ and glass. The light-colored vitreous zone is largely glass, carrying crystals of corundum and $3Al_2O_3.2SiO_2$. The brown crust on the upper surface is made up of thin hexagonal plates of corundum held together by a sodium aluminum silicate glass.

The corundum crystals which drop from the face of the refractories frequently fall into the glass and remain there as stones. A large percentage of the stones in glass examined by the writer have contained corundum from this source.

In the refining end of the tank the action of the soda on the clay refractories results in the formation of other substances as well as the sodium aluminum silicate glass and corundum. In one tank examined frozen drops and stalactites were found depending from the clay blocks which formed the top and sides of the trough through which the glass flowed to the revolving pot (Fig. 7). The principal crystalline constituent of these stalactites was nephelite ($Na_2O.Al_2O_3.2SiO_2$), but corundum and other silicates such as carnegieite (the high temperature form of nephelite),

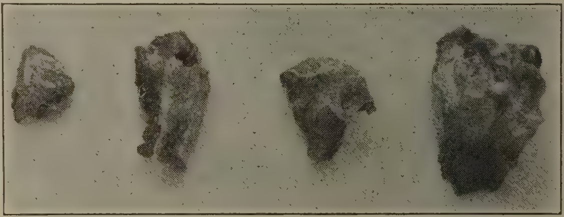

FIG. 7.—Stalactites found hanging from a clay block forming the arch over a flow spout from a bottle glass tank.

melilite and aegirite, were also present. The corundum crystals were very small and showed by their rounded and embayed edges that they had undergone solution. In every case the corundum crystals were enclosed by nephelite. It seems probable that the first substances formed were corundum and glass as in the case just described. As the soda content increased reaction with the glass and the corundum took place to form nephelite or carnegieite, depending on the temperature. It is difficult to account for the fact that nephelite formed in the cool end of the tank while a glass lower in soda formed in the melting end where the atmosphere presumably contained more soda. It is possible that the nephelite could only form at the lower temperature.

Refractories which contain a much higher percentage of alumina than silica should resist the fluxing action of soda better than the usual clay refractories. If the percentage of silica in the refractory is kept low then the amount of sodium aluminum silicate liquid formed would be small compared to the amount of excess alumina. The liquid would be an efficient medium in which the corundum could crystallize but would not be great enough in quantity to drip away from the refractory. The heavy crust of corundum formed on the surface would serve as a barrier against further attacks of the soda. It is essential here as well as in the high alumina refractories for use below the glass line that the bond material shall not vary greatly in composition from the grog. If the bond is high in silica it will be converted into liquid by the soda and will flow away carrying the grog particles with it.

Wherever clay and silica refractories are in contact and exposed to the action of the soda in the glass furnace atmosphere it is found that an unusually great amount of corrosion has taken place. Very often after long exposure a crevice one to two inches wide develops where the contact previously existed. At such places the sodium aluminum silicate glass is formed but is not held in place by a net-work of crystalline material due to the fact that there is no excess alumina to crystallize. It is obvious that a refractory mortar is needed for such contact areas which will not combine with the soda, alumina, and silica on the clay side, or with soda and silica on the silica side to form compounds with melting points lower than the temperatures reached in glass tanks.

Summary

During the solution of the clay refractories exposed to the direct action of the molten glass corundum frequently crystallizes because it is less soluble in the molten soda-lime glass than the aluminum silicates of the clays. High alumina refractories should, therefore, be more resistant to solution by the glass than fire clay refractories. Soda has a most pronounced effect upon refractories exposed to the gases and dusts in

the furnace atmosphere. The effect upon clay refractories is much greater than upon silica refractories. Clay refractories are fluxed rather rapidly, but their resistance to fluxing probably increases with increasing alumina content.

A refractory mortar is needed for the contact between silica and clay refractories which will prevent the reaction between soda, aluminum silicates and silica.[1]

Discussion

MR. AYARS: Do you recommend the use of a bond material of the same character as the grog or a different bond material?

DR. INSLEY: With regard to the question of resistance to glass action, the bond should be of the same composition as the grog but the plasticity of such a high alumina clay would be quite low, difficult to work, and perhaps low in strength.

MR. AYARS: The modern practice, I think, of many of the block makers is to take back not only their own blocks but other blocks that may have been purchased elsewhere.

MR. CARTER: What was the silica and alumina content of the fire clay brick which you spoke of trying, in comparison with silica brick above the glass line?

DR. INSLEY: I did not try them. I simply saw them in the tank. I do not know their composition.

MR. CARTER: I have had some experience which is exactly the reverse of what Dr. Insley refers to, that is, the silica brick wearing away very much more than the clay refractories. This indicates that it makes a great difference what kind of clay refractories you use. Also much may depend upon the nature of the melt and the other characteristics of the furnace. If I were asked for an opinion as to the resistance of the two above the glass line in the furnaces I am familiar with in the making of silicate of soda, I should say that properly selected clay refractories were better for portions of the side walls above the glass line than any silica brick I ever saw.

MR. ROSS: Mr. Carter, did any clay refractories near the silica brick drip upon the silica brick?

MR. CARTER: The condition in which I have seen this was in a crown of a reverberatory furnace where tiles were laid in alternate rings or rows. After the run was finished the appearance of the things was comparable to corrugated iron. In every case the silica brick had retired from the original surface very much more than the clay brick which I was comparing with it.

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[1] Microscopic study of specimens collected during the examination of a used glass tank has been the basis for many of the conclusions in this paper. The writer wishes to express his thanks to Mr. A. Lloyd, Superintendent of Hazel Plant No. 2, of the Hazel-Atlas Glass Co., for the opportunity of examining the tank and to Mr. D. W. Ross of the Findlay Clay Pot Co., for miscellaneous specimens of glass house refractories.

A MEMBER: Wherever any glass is run from clay brick on to silica brick, the latter is wiped away immediately, whereas if the silica brick is subjected to the soda ash and lime that is blown up from the glass they act quite differently.

MR. CURTIS: Did the silica brick where there were alternate rows wear away or spall off?

MR. CARTER: After the run is finished it is difficult to say whether or not the loss is due to spalling or to corrosion. However, in the case of spalling usually it has left some character of surface which indicates that the material has cracked away. The losses would not be regular, due to spalling in certain places and failing to spall in others. In the case I refer to the wear was uniform, from which I infer that it was a matter of erosion and not of spalling.

MR. ROSS: In many window glass plants they use, as the glass men say, "a little bit of salt cake." The tanks in such plants last on the average from 12 to 16 weeks and it is then necessary to remove the upper tier of side wall blocks. On the other hand in some few window glass plants comparatively little salt cake is used in the batch. In these tanks the upper tier of blocks last from about 6 to 12 months.

CHECKER BRICK FOR RESISTING ALKALINE SLAGS[1]

By M. C. Booze[2] and F. C. Flint[3]

ABSTRACT

Checker brick of varying composition were tested by placing them in the regenerators of two glass tank furnaces. The operation of one furnace was representative of those making the usual grade of bottle glass while the other was operated at a considerably higher temperature and with a more corrosive dust.

The amount of corrosion of the checker brick varied directly with the silica content of the brick. Those highest in alumina gave excellent service in the regenerator operating at the lower temperature. In the other regenerator, however, the dust adhered to the high alumina brick and tended to clog the regenerator while it apparently fluxed and drained off of those higher in silica, leaving free passage for the gases.

The brick were tested in the laboratory by making into cones with various percentages of the corrosive dust and determining the fusion point of the cones. The results agree closely with those obtained from the service tests.

Detailed results including partial analyses of the brick and flue dust are given.

Checker brick in regenerators are subjected to rapid temperature changes and often to the action of dust carried over with the burned gases. The dust in the case of glass tank furnaces, for example, is high in soda and lime and, therefore, is corrosive. The temperature attained by the checkers and the amount of fluxing action taking place between the dust and brick depends both upon the operation of the furnace and the composition of the batch in the tank. When the furnace is pushed the temperatures are high and the draft correspondingly great, which results in an increased amount of corrosive dust being carried over.

The checkers are not seriously affected by the temperature changes. The dust, however, is deposited and ultimately causes failure either through excessive corrosion due to high temperatures and a rapid solvent action, or by sintering sufficiently to cause the brick to stick together. The practice varies in different plants, but it is usually the case that the dust deposit becomes sufficient from time to time to clog the openings in the regenerators and this requires that the brick be taken out and cleaned. If the dust has fritted to the surface, it must be chiseled off and this results in considerable breakage. If the brick are stuck together by the slag, they must be knocked apart and the salvage is small. It is advantageous, therefore, to use material which is not rapidly attacked by the dust.

Effect of Composition and Structure of the Brick

In order to determine the service which could be expected from brick varying in chemical and physical composition, several kinds, ranging from silica brick to ones high in alumina and from a medium to a very dense structure, were placed in the top of regenerators of two tanks making products which differed considerably in composition. The operation varied considerably also; that from which the No. 1 dust was taken was forced to maximum capacity with resulting high temperatures;[1] the furnace from which the No. 2 dust was taken was not forced and both the operation and dust composition of this furnace is considered as being fairly representative for a large number of tanks making bottle glass.

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[1] Presented at the Atlantic City Meeting, February, 1924 (Refractories Division).

[2] Senior Fellow, Refractories Manufacturers Association Fellowship, Mellon Institute of Industrial Research, University of Pittsburgh, Pittsburgh, Pa.

[3] Chief Chemist, Hazel-Atlas Glass Company, Wheeling, W. Va.

In the No. 2 regenerator the dust fused to a glass only when in contact with highly siliceous material, while it was still dry and could be readily removed from the checkers high in alumina. The brick were taken out of this regenerator for inspection after seven months' service. As previously indicated, those high in alumina had given the best service, the one listed here as No. 1 being almost 100% salvable. Those somewhat lower in alumina had not been actively attacked, but the dust appeared to fuse to the surface sufficiently to make them stick together and difficult

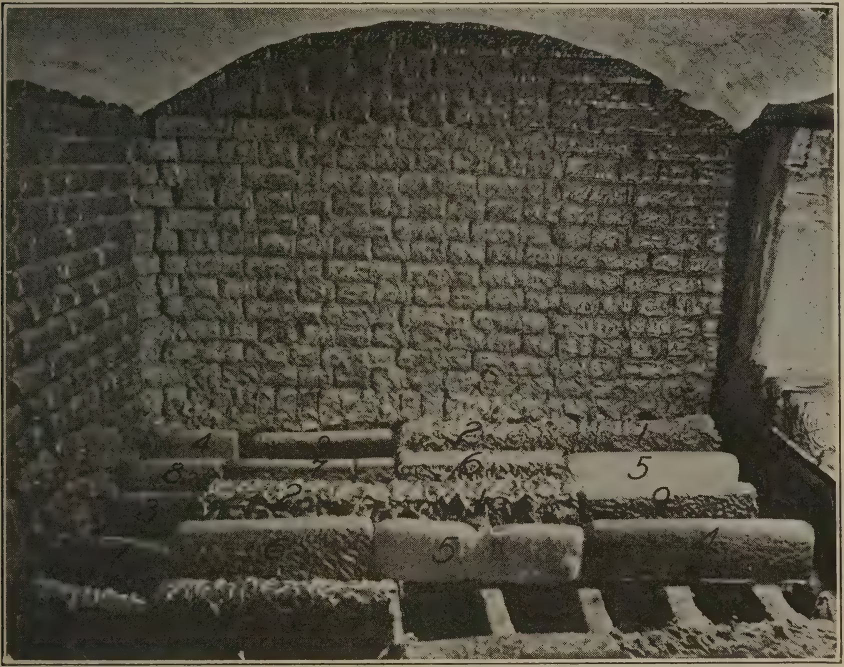

FIG. 1.

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[1] The temperatures of the top checker brick were measured with an optical pyrometer and found to vary from 2000°F to 2200°F. The temperatures in the No. 2 regenerator varied from 1800°F to 2000°F.

to clean. Those high in silica had been attacked to a sufficient extent that the sides presented in places a smooth, glassy appearance and in others the dust had adhered to this glass and built out for a distance of one or two inches.

The photograph shown in Fig. 1 was taken in the regenerator from which the No. 1 dust was taken and shows the condition of the checkers here after eight months' service. The numbers on the photograph identify the various kinds of brick in accordance with the data presented in Table I. It may be noted that 1 and 2 which are high in alumina are coated with a crust of partially fused slag, while the pieces numbered 3, 4, 5, 7 and 9 have been much more corroded; 6 and 8 are not badly corroded. These have a high alumina content as compared with the average fire clay brick. The pieces shown in the photograph were not located in the hottest portion of the regenerator and where higher temperatures had existed, the differences were more pronounced than is evident here, the more siliceous brick having fluxed almost entirely away. While there was

TABLE I

Brick no.	Porosity %	Silica %	Alumina %	Fusion point cone	% Slag	Fusion point with No. 1 slag	% Slag	Fusion point with No. 2 slag	Service in regenerator with No. 1 dust	Service in regenerator with No. 2 dust
1	29.1	34.7	58.6	Above 33	5	cone 33+	7½	cone 30	Excellent	Excellent
					10	cone 32	15	cone 13		
					20	cone 5				
2	30.3	39.7	54.1	32–33	5	cone 32	7½	cone 30	Excellent	Good
					10	cone 20–26	15	cone 12		
					20	cone 5				
3	27.4	45.4	40.5	30–31	5	cone 27	7½	cone 16	Poor	Poor
		High in			10	cone 15	15	cone 10		
		Fe_2O_3			20	cone 5				
4	32.4	72	25	30	5	cone 20–26	7½	cone 15	Very poor	Poor
					10	cone 18	15	cone 10		
					20	cone 8				
5	29.3	94	2	30	5	cone 20–26	7½	cone 15	Very poor	Poor
					10	cone 17	15	cone 15		
6	22.1	49.7	44.7	32–33	5	cone 31	7½	cone 20–26		
					10	cone 27–28	15	cone 12	Fair	Good
7	14.5	52.7	41.1	32–33	5	cone 29–30	7½	cone 20–26		
					10	cone 26–27	15	cone 10	Fair	Good
8	25.9	47.1	44.6	32–33	5	cone 30–31	7½	cone 20–26		
					10	cone 27–28	15	cone 11	Fair	Good
9	21.7	59.0	37	31–32	5	cone 28–29	7½	cone 19	....	Good
					10	cone 26	15	cone 10		
10	....	56.4	35.5	31–32	5	cone 28	7½	cone 19	Fair	Good
					10	cone 26	15	cone 10		
11	25.4	49.7	41.5	32	5	cone 28	7½	cone 16	Fair	Good
					10	cone 26	15	cone 9		

sufficient reaction between the high alumina brick and the dust to allow a crust to build out from the sides which would tend to clog the regenerators this condition is to be preferred to rapid erosion.

Comparison with Laboratory Slag Test

In order to determine whether a laboratory slag test would give parallel results, cones were made from mixtures of the various kinds of checkers with the dust which caused corrosion. These were fused against standard cones. The results obtained, together with the silica and alumina contents of the various checkers and compositions of the two dust samples taken from the regenerators, are given in the tables.

It is evident that there is a general relation between the amount of slagging action taking place in the regenerators and the fusion point of the mixtures of slag and brick.

Although the fusion point of the No. 1 slag or dust is very low, it does not appear to lower the fusion point of the brick as much as the No. 2 slag.

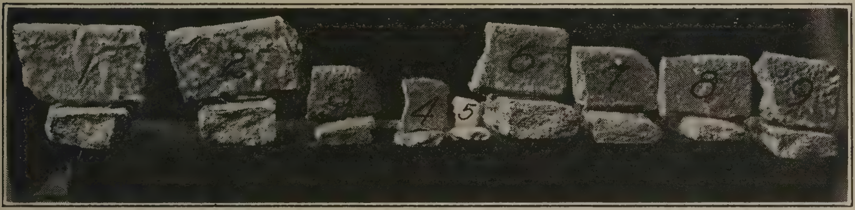

FIG. 2

The fact that the checkers in the regenerator from which the No. 2 slag was taken are giving longer service than those in contact with the No. 1 slag is due to the former being operated at a considerably lower temperature than the latter.

TABLE II—INCOMPLETE ANALYSES OF DUST SAMPLES FROM REGENERATORS OF THE TWO TANKS

	Silica	Alumina	Lime	Magnesia	Alkalies	Fusion point
No. 1	40.60	12.60	11.36	7.15	22.83	Below cone 1
No. 2	3.49	2.03	44.82	32.51	11.97	Cone 20–26

The percentages are computed on an ignited basis, there being respectively 10.4 and 15.9% ignition loss on the two samples.

Discussion

MR. AURIEN: What are the sizes of those tile?

MR. FLINT: All tile were 3 x 6 x 18.

MR. CURTIS: In a pot furnace where you have no fluxing condition which would you recommend, a clay tile or a silica tile?

Mr. Flint: I do not believe this work covered that enough to really give answer to your question. This is just testing the fluxing plus the heat.

Mr. Carter: In connection with what has just been said about that type of tile which somewhat wastes away, it is possible for the melted material flowing down toward the bottom of the system to go through the system for a certain distance. It suddenly freezes up, so that although the upper portion of the system remains perfectly clear the bottom is perfectly closed. If there is heat enough to carry down through, it is all right. If there is not, be rather wary of tile which melts freely under the action of this dust.

Mr. Flint: These tile which showed a mild amount of fluxing were not by any means bad tile. They were standard checker tile. I cautioned against taking this as a standard for your own tank. This particular tank operates at an average of 2700°; it varies from 2650 to 2750°. The top of the checkers are fairly close to the level of the glass and it comes rather close to the fire. The checkers at the bottom are approximately 1600°. That particular tank will not freeze up at the bottom of the checkers. The third tank from which we have not yet been able to take the tile out has been running nearly a year now, which is a good record. This last tank runs the checker chamber at the bottom of about 1400, and under these conditions it would very likely freeze at the bottom and we would have to make a different set of conclusions. For that reason we chose three different tanks and three different conditions in our practice.

Mr. Aurien: Are these tile made up of special mix?

Mr. Flint: No. They were purchased in the market from standard manufacturers and taken from their stock, but there was one special mix in there.

Mr. Aurien: Was this equivalent to No. 1 common brick?

Mr. Flint: Equivalent to high grade checker tile. One of them, particularly, is one that we used in a good portion of our tanks. We were determining this with the idea of being able to purchase, if desirable, from the manufacturer all we want of any grade if it was found to stand any better than any others. We could not do that if it were something special.

A QUANTITATIVE LABORATORY SLAG TEST

By F. H. Norton[1]

ABSTRACT

A laboratory slag test is described capable of giving quantitatively the resistance of refractories to slags. The method consists in continuously spraying powdered slag onto the hot specimens and allowing it to run off. The advantage of this test is the rapidity and small expense with which relatively accurate results can be obtained.

Review of Methods

A laboratory slag test should first measure the resistance of refractories to the action of slag in such a way as to give results comparable with those obtained from the same refractories in service; second, the test should give quantitative results that can be checked to a reasonable degree of precision; and third, the results should be obtained rapidly and with slight expenditure.

Slag Penetration

Some of the first slag tests merely measured the penetration of the slag into the heated refractory. This was accomplished either by immersing a complete brick in a bath of molten slag[2] or by melting the slag in a fire-clay ring molded onto or cut into the surface of the refractory to be studied.[3] These tests did not simulate actual conditions. The slag was not in motion, and therefore the chemical action between the slag and the surface of the refractory was very slow and little if any of the surface of the refractory was removed. The resistance of a brick to slag is not dependent on the penetration. Some of the best slag-resisting brick are porous and soon saturated with slag. Some other brick show no penetration of slag, yet moving slag eats them away rapidly.

Mixing Powders of Refractory and Slag

Another type of slag test[4] is conducted by grinding known proportions of the refractory and the slag together, and measuring the melting point of the resulting mixture. This method gives a good insight into the chemical action between the slag and the refractory. It does not, however, simulate actual conditions and takes no account of abrasive action.

Flowing of Slag in Groove over the Refractory

Professor G. B. Wilkes in this laboratory noticed that slag in motion executed a comparatively rapid cutting action on the surface of the refractory. A brick was heated in a gas furnace to the required temperature. Slag was dropped steadily onto the top of the brick, melted and run down a groove, cutting away a portion of the refractory quite rapidly. The abrasive action of slag was simulated. The brick particles which had been loosened by chemical action were washed away. The moving slag supplied fresh material to the surface, accelerating the chemical action. These tests gave satisfactory relative results which agree well with service tests.

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[1] Babcock & Wilcox Research Fellow, Division of Industrial Coöperation and Research, Mass. Institute of Technology. Presented at the Atlantic City Meeting, Feb., 1924 (Refractories Division).

[2] G. H. Brown, "A Method of Testing the Corrosive Action of Slags on Fire Brick," *Trans. Amer. Ceram. Soc.*, **18**, 277 (1916).

[3] A. S. T. M., Tent. Stands. (1922).

[4] Howe, Phelps and Ferguson, "Action of Slag upon Silica, Magnesite, Chrome, Diaspore and Fire Clay Refractories," *Jour. Amer. Ceram. Soc.*, **6** [4], 589 (1923).

Revolving the Refractory in Bath of Slag

Recently a test has been devised for measuring the action of glass or slags on various refractories, by lowering a rod of the refractory into the bath of slag and revolving it at a given rate of speed.[1] The decrease in diameter of the rod gives a quantitative value for the action of the glass or slag. This method should be quite satisfactory for the low temperatures used in glass work, but at temperatures over 3000°F there is great danger of contamination of the melt by the container and the suspended rod will probably be too weak to support itself.

Dipping and Draining

An attempt was made by the author some months ago to make a quantitative slag test by dipping a small specimen into a bath of molten slag, then taking it out and letting the slag run off and repeating this process until the refractory had been reduced in size. This method was unsuccessful because no container could be found to hold the slag at high temperatures without serious contamination, and because the specimens did not have the required strength to support themselves when being removed from the bath.

Introduction of Slag through Burner

The conditions desired in an ideal slag test are an even flow of slag over one or more faces of the specimen; and an even flow cannot be maintained by introducing the slag at one point and letting it run down, for a groove is soon started and all the slag will run down it. This groove deepens rapidly until there is little action at any other place. After a great deal of experimenting it was found possible to obtain a very even action by introducing powdered slag into the air line of the burner, from which it was carried down into the test furnace with the flame, and formed an even and constantly renewed coating over the test specimens. This method has now been in use for several months and has proved so successful that it is thought a description of it will prove of general interest.

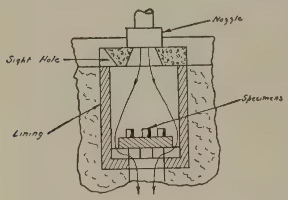

Fig. 1.—Section of furnace.

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[1] Charles I. Rose, "A Proposed Method for Studying the Attack of Molten Slags and Glasses upon Refractory Materials," *Jour. Amer. Ceram. Soc.*, **6** [12], 1242 (1923).

The Furnace

A section of the slag test furnace is shown in Fig. 1. The flame is blown downward from the nozzle directly onto the specimens which are supported on a disk. The slag which is introduced into the pipe a short distance above the nozzle is sprayed evenly over the disk where it immediately melts onto the surfaces and gradually flows out through the bottom of the furnace. The outside of the complete furnace is shown in Fig. 2 where the reservoir for the slag and the feeder is visible.

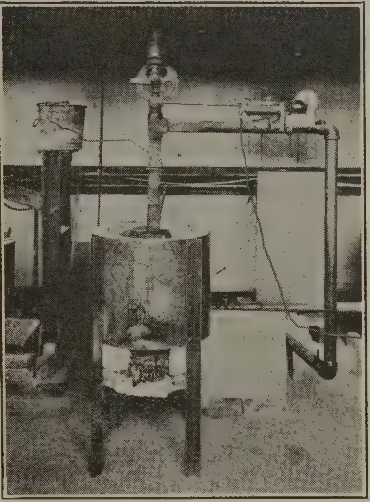

FIG. 2.

Method of Operating

The slag is ground to pass a 20-mesh screen and a given weight of it is placed in the reservoir. The speed of the feeder is then regulated so that a predetermined amount of slag passes through the furnace in one hour, which is the time used in most of the runs. In order to be sure that all of the specimens in the furnace, which may number as many as eight, received the same amount of slag, a set of identical specimens was placed on the disk and a run made. The resulting action of the slag was, as near as could be determined, exactly the same on all specimens as can be seen in Fig. 3, which shows a set of identical specimens after a one-hour test.

The temperature of the furnace can be easily regulated from the melting point of the slag, which is usually about 2300°F up to 3200°F, or even higher if desired.

Refractory Specimen

The specimens used in the tests are either one-inch cubes or cylinders one inch in diameter, and one inch high. This size is convenient and appears to be large enough to give satisfactory results. The cubes are cut with a carborundum saw, and the cylinders are molded and fired or cut out of a brick with a one-inch diamond drill.

The volume of the specimen is measured before the run by placing it in a small cup and covering it with sand. The difference in volume between the sand in the cup and the volume of the cup readily gives the volume of the specimen. After the run the slag is allowed to drain off from the surface of

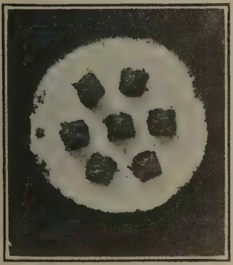

FIG. 3.

the specimen, its volume is again measured, and the percentage of the original volume remaining is computed.

Results

One set of tests is given here to show the precision of this method, and to indicate how important temperature is on the action of slag. The specimens tested were: A, B, C—specimens of three kinds of high-grade fire-clay brick, D—a bauxite brick, E—a silicon carbide brick, F—a magnesite brick. The slag used was a coal ash slag with composition approximately SiO_2, 40.9%; Fe_2O_3, 29.7; CaO, 6.3; MgO, 0.9; Al_2O_3, 22.3.

The results of this test are shown in Fig. 4 where the per cent of each specimen remaining at the end of the test is plotted against temperature. It will be noticed that there are a number of check runs, and that the greatest distance of any point from the mean curve is 5%, and in most cases they are within 1 or 2%.

Relation of Temperature to Erosion

It is interesting to notice that a brick which stands the slag test at low temperature may have the least resistance at high temperature; so that one should be very careful in judging the characteristics of a refractory when it is slag tested at only one temperature. For example, the magnesite brick is apparently unaffected at 2600° while it is practically destroyed at 2900°. The bauxite brick shows the same tendency, but to a somewhat less degree, while the silicon carbide brick shows a practically constant erosion by the slag for all temperatures.

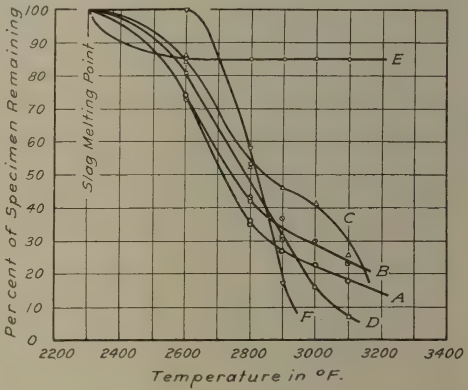

Fig. 4.—Slag resistance of various refractories.

Results Simulate Service

The results obtained by this slag test on the whole check up well with the service of the refractories in actual use. However, there have been a few cases where a specimen showed a somewhat higher or lower resistance than service conditions indicated. This is probably due to the fact that the small specimen is heated evenly throughout, while the brick in service are heated only from the surface exposed to the slag. These discrepancies are small and infrequent and should not be a serious disadvantage.

The chief advantage of this test lies in the rapidity with which it can be carried out, even at high temperatures. Three to six runs can be made in a day with as many as eight specimens in each run.

Cambridge, Mass.

SOME COMBUSTION PROBLEMS IN GLASS MAKING[1]

By C. D. Smith

ABSTRACT

For a plant operating on producer gas and with possibilities for results that approach present best practice care must be exercised to see that not only producer gas equipment of recognized merit is installed but that gas mains are of ample size with adequate facilities for cleaning or burning out, that valves are large enough to take care of requirements and with minimum resistance to exit gases and that facilities be provided for gas checker temperature regulation as well as air regulation.

The consumption of fuel in the glass industry, when expressed as coal or its equivalent, totals a large tonnage and when we realize that nearly if not quite 90% of its potential heat value is dissipated as stack and radiation loss, the heat energy waste is impressive.

It would seem at first thought that the fuel economist would here find a fruitful field in which to labor but, as in many other furnace operations, the temperature range between working limits is so narrow and at such a high potential that only a relatively small percentage of the heat developed can be absorbed by the product of the furnace. Any gain in fuel economy over present best practice comes only in fractions of a per cent and as a result of painstaking care and earnest endeavor. It is only within comparatively recent years that fuel economy has been given serious thought and in the glass industry there are many plants which from the standpoint of fuel economy do not equal present best practice.

By no means do all of the combustion problems have to do with fuel economy. In some cases fuel efficiency would gladly be sacrificed could uniform and satisfactory furnace conditions be assured. Nevertheless the fuel engineer is ever looking for decreased fuel consumption and sometimes his zeal in this direction oversteps other primary considerations, namely—output of product. But he would indeed be remiss in his efforts should he consider results obtained as satisfactory even though they compare favorably with average practice. He must constantly be on the lookout for that fraction of a per cent. There is no doubt but that the best economies of today will be still better tomorrow and without sacrificing quantity or quality in product.

Perhaps a discussion of combustion problems will appear more to the point if the writer gives somewhat in detail a few personal experiences that are typical.

Importance of Air Adjustment

(1) A forty-ton continuous tank had just been rebuilt for producer gas and therefore had double checkers. It was operating, however, on natural gas and although the furnace conditions were considered excellent, with

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[1] Presented at the Atlantic City Meeting, Feb., 1924 (Glass Division).

glass satisfactory, the gas consumption was excessive. The feeling seemed to prevail that the high gas consumption was due to the construction for producer gas and that it was unavoidable whenever the tank was operated on natural gas. The following features were noted:

No stack damper and a particularly large flue leading from the furnace to a high stack.

A large air valve wide open and with no provision for regulating air.

Gas valve also acting as an air valve.

Dampers were provided in the flues leading from the checkers to the valves and draft regulation was accomplished by the adjustment of these dampers.

As a preliminary step, four flue gas samples were obtained and analyzed. The results are given below in "Flue Gas Samples before Air Adjustment."

Flue Gas Samples

Before air adjustment Sample no.	CO_2	O_2	CO	After air adjustment Sample no.	CO_2	O_2	CO
1	7.5	10.0	0	5	12.0	4.8	0
2	5.6	15.8	0	6	9.8	4.0	0
3	4.8	12.0	0	7	12.1	5.3	0.1
4	6.4	9.8	0	8	10.1	2.8	0
Max.	7.5	15.8	0	Max.	12.1	5.3	0
Min.	4.8	9.8	0	Min.	9.8	2.8	0
Av.	6.4	11.9	0	Av.	11.0	4.2	0

From this analysis the excess air figures 123%, which of course is excessive.

An air valve cover with means for regulating it and a stack damper were installed. After these were regulated in conjunction with the checker dampers already mentioned, four more flue gas samples were obtained and analyzed. The results are given above in "Flue Gas Samples before and after Air Adjustment."

This is clearly much better from the standpoint of combustion and with these results the excess air figures 23%.

The furnace temperature began to increase and within a day or two the gas pressure was decreased from 8 oz. to about 5 oz. Gas meter readings were recorded regularly at the beginning of each eight hour shift. For the thirteen consecutive shifts preceding the change in air adjustment the average gas consumption per shift was 148100 cu. ft. and for fourteen consecutive shifts following the adjustment it was 129300 cu. ft., a reduction of 18800 cu. ft. per shift or 56400 cu. ft. per day; a saving of over 12.5%.

Case of Scarcity of Air

(2) Frequently it is a scarcity of air rather than a surplus that contributes to furnace difficulties and limits output; expecially is this true of the older installations. In the following case an insufficient air supply kept the furnace at a rating considerably under its normal capacity.

This was a continuous tank operating on producer gas and with a fuel consumption considered high for its output. It was believed that the producer gas or the gas producer equipment was at fault since with natural gas the tank performance was much better. This could have readily been the case for then both air and gas valves and checkers are available for air.

Flue gas samples were taken on both sides of the tank. The analyses are given in the following table:

Flue Gas Analyses

Fuel—Producer gas

Sample no.	CO_2	O_2	CO	Sample no.	CO_2	O_2	CO
1	16.4	2.3	0.0	7	17.0	1.9	0.0
2	17.0	1.8	0.0	8	16.6	1.8	1.2
3	16.6	2.4	0.4	9	16.6	2.1	0.0
4	18.0	0.6	0.6	Max.	18.0	2.8	1.2
5	17.8	2.8	0.0	Min.	16.4	0.6	0.0
6	16.5	2.5	0.0	Av.	16.9	2.0	0.2

The air valve was wide open so the furnace was taking all the air it could get. From the foregoing analyses additional air would have been an advantage. It is also quite clear that the furnace could not have taken on additional load.

An analysis of the producer gas was made at this time with the following results:

CO_2	6.0	H_2	13.6
Ill.	0.4	CH_4	2.8
O_2	0.2	N_2	52.8
CO	24.2		

From the average flue gas and the producer gas analyses the excess air was computed and found to be only 15.1%.

With producer gas 30 to 40% excess air is considered good practice.

The single sample of flue gas was taken from the bottom of the gas checkers at a point just above the rider arches. This gave the following results:

CO_2	9.9
O_2	9.7
CO	0.0

This is in marked contrast with the flue gas samples taken at the exit ports of the furnace and shows the extent to which infiltration of air may take place through the checker walls. It also emphasizes the importance of taking flue gas samples for control work as near the exit ports of the furnace as possible.

Draft readings were taken in inches of water at various points and these are shown in a diagram. The draft pressures observed on this tank were as shown in Fig. 1. In Fig. 2 draft pressures are indicated as observed in a tank operating satisfactorily. Although the furnace in Fig. 2 is considerably larger than the furnace in Fig. 1 and has a stack with a greater draft, as well as a much larger air valve, it will be noted that the draft on the furnace side of the stack damper is less than the corresponding draft in the smaller furnace, but that the draft in the flues leading from the checkers to the stack is less in the smaller furnace.

The resistance of the air valve to the passage of the waste gases in Fig. 1 is .37 of an inch, or over 50% of the stack pull, while in Fig. 2 it is .22 of an inch or about 27% of the stack pull. Unfortunately such conditions are general.

Even in new installations with extra large valves the resistance of the air valve to the flow of the exit gases is from 25% upward of the stack pull. Referring again to Fig. 1, it will be noted that the draft at the bottom of the air checker on the inlet side is .04 of an inch; although this is not very much it is more than would prevail in a flue of ample section, such as this, and a large valve wide open. It means that the inlet air was restricted at the air valve. This draft of .04 at the base of the air checkers has a further significance. With the air restricted as it was at the air valve and with ample uptake flues from the top of the checker chamber the drop in pressure in the flue leading to the checker would be considerably more than .04 which indicates that the uptake flues are too small. This tank had a very high crown, it being at the center, 6 feet 5 inches from the metal line, inside measurement. It also had high narrow ports 30 inches high x 24 inches wide. For the satisfactory combustion of producer gas both of these conditions are unfavorable.

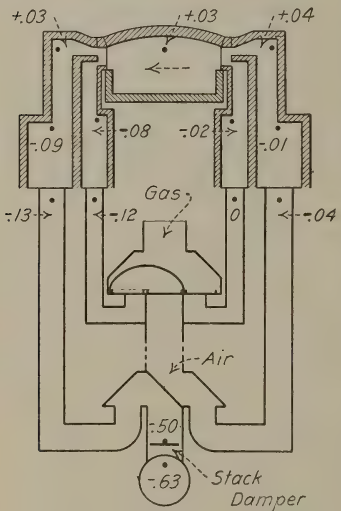

Fig. 1.

The furnace was rebuilt and the crown lowered about 17 inches, the ports were made 30 inches wide by 18 inches high; the uptake flues were increased in size by about 50% and a much larger air valve was installed. After these changes were made the tank functioned exceptionally well and made excellent glass at more than rated capacity.

A Case of Faulty Gas Mains

(3) At another plant running on producer gas the furnace operation was very unsatisfactory and going from bad to worse. The gas was

unsteady and at times it almost disappeared from the furnaces. At other times there was an abundance, the furnaces were flooded with gas and tongues of flame darted from every crack and crevice until it could be checked. As expressed by the furnaceman, "The gas is no good any more and when there is a plenty it has no kick; we cannot make glass with that stuff." The superintendent of the plant said the situation was indeed serious; his feeling was that the producers were at fault and that he would be much better off with a battery of old style hand poked producers. There were three full mechanical producers of a standard make.

For a day or so the writer made no attempt to change any of the conditions but to observe for himself and get first hand information concerning existing conditions and operating details. Much that had been said seemed to be true; the gas did "come and go" in the furnaces and as the furnaceman said: "When it did come it had no kick." Furnace temperature increases came slowly and with difficulty, particularly above 2350°F.

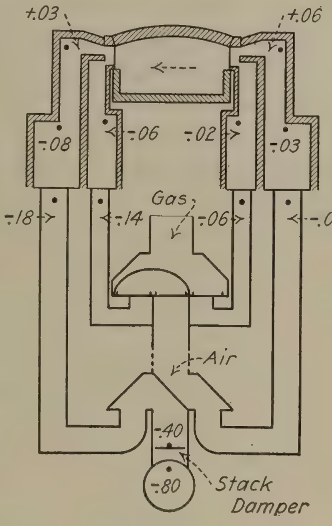

FIG. 2.

In order to determine the pressure variations of the gas a manometer was placed on the gas main in the producer house and inside of twenty minutes the gas pressure varied from $^1/_2$ inch of water to $2^1/_2$ inches, a variation amply sufficient to account for all of the "gas come and go" in the furnaces. Under normal conditions the pressure variation in a gas main should not exceed 0.2 of an inch. This information had no significance whatever to the gas makers.

Two samples of producer gas were obtained for analysis but they were not completed due to failure of the gas to explode in the analysis apparatus: presumably the gas was too poor to explode. The CO_2 content, however, was determined and this showed 10.2 and 13.0% respectively; ample evidence of exceedingly poor gas.

Under conditions of good operation the CO_2 content will not exceed an average of 6%. The temperature of the gas leaving the producers was exceptionally low, rarely going above 1000°F. The producers were also badly clinkered, the side walls being covered with dense clinker to a thickness of approximately 12 inches. The producers were equipped with steam jet blowers which were working at an abnormal pressure of 80 to 90 pounds of steam. These blowers were so situated that inspection was difficult and from the condition they were in it is doubtful if they ever had been; some of the air passages were entirely stopped up with ash and dirt and in the others there were varying amounts so that for the blower as a whole the air opening was less than 50% of that of a clean blower. With this condition of the blowers and 90 pounds steam pressure it is no wonder the gas was lean and the producers cold. The gas producers were situated some distance from the furnaces and consequently the gas mains were long. With a gas velocity of 10 feet per second as a basis for calculating gas main sizes, all of these lines were very much under size; they were also poorly equipped with burnout connections and dust legs and other facilities for cleaning out. On the first burnout day after the writer arrived he saw a four-foot gas main 60 feet in length, two-thirds full of soot and with no cleanout doors or dust legs from one end to the other. It took 12 hours to burn out this line.

In the layout and operation of this plant there was much to be desired. To make of it an operating installation that would compare favorably with the best practice, called for an entirely new system of gas mains with ample burnout connections and facilities for cleaning out. Such a system was installed. No change was made in the type of producer equipment but each producer was overhauled and an additional unit was installed. A pressure regulator was also installed to maintain a uniform gas pressure.

Since the completion of these alterations this plant has operated in a very satisfactory manner. The gas has been of good quality and of uniform pressure, thus doing away with the "come and go" of the gas in the furnaces. There has been no difficulty in bringing up the temperature of any furnace to a desired point within a reasonable period of time. The burnout period has been reduced from 12 or 14 hours approximately to $2^1/_2$ hours, and in glass output quality has been greatly improved while the quantity has been increased by over 25%.

Too Much Clinker Due to Faulty Blast Hood

(4) In response to distress signals from another plant it was found that two small continuous tanks running on producer gas were giving considerable trouble from seedy glass and temperature variations. Much ware was being lost and frequently several shops had to suspend operations until the tanks could regain temperature.

Three 10 foot producers working to their limit were unable to hold the tanks in good working condition. Analysis of the gas showed it to be of very poor quality and an investigation of the producer interior through the use of a poker revealed that the bottoms of the producers were literally packed with dense hard clinker. The producers were of an old hand poked type that had been equipped with mechanical agitation but with hand feed. The inside walls were straight from top to bottom and without the usual bosh; this facilitated the removal of ash to some extent but it also had the disadvantage of being responsible for many slips of the fuel bed into the water seal at the bottom, while ash and clinker were being removed. When such movements take place the fuel bed is unavoidably broken up and it is of necessity some time before good gas making conditions can be restored.

One of the producers was taken off the line for a more thorough internal examination. All of the ash was fused into a dense clinker of which there was an accumulation 3 to 4 feet in thickness. Through this mass there was only here and there a channel or chimney through which the blast reached the fuel bed. It was thus very much localized and one of the most essential features for good producer operation, namely—uniform distribution of air blast, was eliminated. The blast hood or tuyère was found to be of an obsolete type; it was of large diameter and all of the openings that had previously existed at the top and sides were completely stopped up with ash and clinker so that all of the blast entering the tuyère had to find exit under its lower outer edge and comparatively near the walls of the producer. This lower edge was only three inches above the water level of the seal at the producer bottom and it is not unlikely that this close contact had the effect of condensing at least a part of the steam in the blast thus aggravating an already bad condition.

The old blast hood was discarded and one of improved pattern installed in its place. The new blast hood was placed 15 inches higher up in the producer. The steam nozzle of the jet blower while large enough for these producers with hand poking was not large enough for the increased capacity of the producers made available by mechanical agitation. This nozzle was accordingly drilled out from $^5/_{16}$ inch to $^7/_{16}$ inch. All of the producers were overhauled in the same manner. Although using the same coal, clinkers were eliminated, gas of good quality was made and in ample quantities for the demands of the tanks and with a saving in coal of from 3 to 4 tons per day. The tank temperature was readily controlled and the seedy glass disappeared.

Another Case of Air Deficiency

(5) Air deficiency was a matter of considerable importance in the following case:

A continuous tank operating to capacity produced during a period of seven weeks an average of $50^1/_2$ tons of glass per 24 hours but in doing so it consumed large quantities of producer gas which burned with a flame extending through the checkers and the flue to the stack. The air valve was of the maximum size made and there was no reason to believe it was too small. The air checker uptake flues, however, were undersized and were clearly the points of restriction. The fire was turned out and the uptake flues enlarged 75%. During the four weeks following the tank averaged 64 tons per day on appreciably less fuel.

Some Gas Producer Problems

Combustion problems in glass making of the future will have to do very largely with producer gas. It is therefore important that we give attention and study to all the characteristics of this fuel.

The contempt with which the seasoned gas maker sometimes greets a reference to gas analyses is not altogether without reason. He has heard a furnaceman complain of the gas when an analysis showed it to be of average quality and he has heard him say, "The best ever old man," when the analysis showed it to be even below average quality.

An illustration of these characteristics is shown in the following plant operation:

The Flame

A single producer with mechanical feed and mechanical agitation was furnishing gas for a small continuous tank; the fuel consumption was about 20 tons per day. The coal feed mechanism did not permit of fine adjustment but would feed at the rate of either 14 or 28 tons per day; it was therefore necessary to change from one feed to the other to get the required 20 tons. Occasionally there was an overcharge of coal and then all feed was cut off for several minutes. At such times the furnaceman invariably went to the producer plant and reported "poor gas." Samples taken during "coal on" and four minutes after "coal off" showed no essential difference in the analysis but there was a difference in the character of the flame in the tank. When a producer is working under normal conditions with coal feeding at regular intervals the gas atmosphere has a smoky appearance, generally of a slaty color but sometimes with a yellowish tinge. This smoke or visible part of the gas is principally tar vapor and in gas house parlance is called "fog." These tar vapors are hydrocarbons of an order probably approximating that of naphthalene, $C_{10}H_8$; they readily condense when a sample of gas is obtained and do not show up in an analysis but they do add heat value to the gas and because of their high carbon content they give a luminous characteristic to the flame so much desired in tube welding furnaces and which the writer believes is highly desirable in the glass tank. Many gas makers judge the gas by the color of the "fog." If the coal feed is shut off the "fog" generally disappears in a very few minutes and the gas atmosphere becomes clear; some of the best producer gas analyses ever made have been from samples taken in a clear gas atmosphere.

A tube welding furnace is much more sensitive to flame conditions than a glass tank for the thin walled tubes not only have to be heated very carefully but in a neutral or slightly reducing atmosphere. The heating tubes are watched constantly and the welders soon become expert in their ability to detect flame variations and their effects upon the tubes.

That a gas analysis is not a true or complete indication of the gas requirements for a welding furnace is apparent from the following table:

No.	Poor 1	Good 2	Poor 3	Good 4	Poor 5	Good 6
CO_2	7.5	6.4	7.4	7.7	6.8	6.4
Ill.	0.6	0.4	0.6	0.5	0.8	0.7
O_2	0.0	0.4	0.0	0.1	0.4	0.1
CO	21.4	24.0	23.5	23.7	23.4	24.6
H_2	12.6	11.4	12.9	13.5	15.6	13.2
CH_4	3.8	3.3	3.5	2.1	2.7	3.3
N_2	54.1	54.1	52.1	52.4	50.3	51.7
	100.0	100.0	100.0	100.0	100.0	100.0
B.t.u.	156.5	152.5	161.4	147.3	162.9	164.1

The gas was reported as being fine when samples 2, 4 and 6 were taken and as being very poor when samples 1, 3 and 5 were taken.

There is a considerable variation in the B.t.u. values and yet the lowest heat value gas was reported as fine while with one of the highest heat value samples the gas was reported as very poor.

Heat Value A. G. Witting, of the Illinois Steel Company in a paper before the Association of Iron and Steel Electrical Engineers refers to "the error so commonly committed in judging the quality and the heating value of producer gas from an analysis of the fixed gases it contains, neglecting the tarry vapors, something that should not be excused with the inability to determine their amount." He calculates that the heat value of the tarry vapors in producer gas from Indiana coal is over 11% of the total heat value of the gas. If this is true and since the tarry vapors are given off soon after the coal is charged into the producer, then, with intermittent firing, the effective or real heat value of the gas may vary as much as 10% although the gas analysis might show a particularly uniform gas. It then follows that the coal fed into a producer should approach as nearly as possible a steady uniform stream.

Luminosity There is a difference of opinion in regard to the value of luminosity in producer gas but the writer firmly believes that it is of the highest importance especially in glass and tube welding furnaces. His experience with cold clean producer gas from which all tarry vapors have been removed leads him to believe that it takes from 30 to 40% more in B.t.u. to operate a tank to capacity with clean gas than it does with raw gas.

Referring to the diagram of an ordinary glass tank (Fig. 3) and assuming that air and non-luminous gas are coming from their respective ports and burning as they pass through the furnace, I think it will be conceded that a very large proportion of the gases making up the products of combustion will pass through and out without coming in direct contact with either the crown of the furnace or the surface of the glass. Let *A* represent a small volume of such gases. Since it does not approach any of the characteristics of the "perfect black body" it cannot radiate its heat as it otherwise would. Since it does not come in contact with heat absorbing surfaces it does not give up its heat by convection. Since it is surrounded by other similar volumes of the same temperature there is little chance of heat transfer by conduction. But, place within that volume the innumerable little carbon particles that are set free when tar vapors and other hydrocarbons burn, "perfect black bodies" that they are, and it will radiate its heat and give that so-called soft and soaking heat which "looks" beneath the surface of the glass and gives it a uniform nature; and which gives the characteristic flame in a welding furnace that makes the welder smile. It is very questionable with non-luminous gas even with ports so constructed as to make the flames impinge on the surface of the glass so as to give up its heat by convection that the results would be satisfactory. The heat is localized and thereby gives rise to uneven temperatures and hence a glass of several natures.

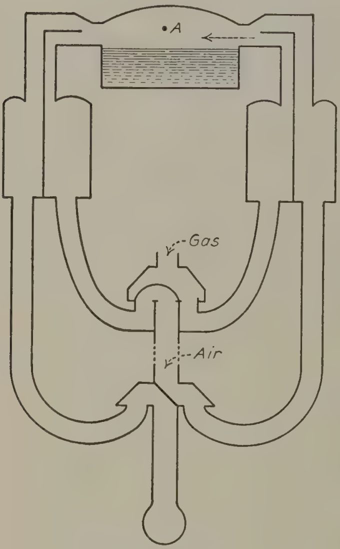

FIG. 3.

Gas Checker Temperature Control

Although tar vapors and other hydrocarbons may leave the producer in a satisfactory manner their value as illuminants is often destroyed by passing them through overheated gas checkers. The effect of gas checker temperature control is shown in the following operation:

The performance of a glass furnace operating on producer gas was considered to be of a good average yet it had its ups and downs, its variation in heats, and a noticeable "come and go" to the gas in the furnace. A systematic study of checker temperatures resulted in a controlled gas checker temperature of approximately 1450°F. At this temperature the hydrocarbons were not decomposed but were carried into the furnace and there utilized to the best advantage. This resulted in greatly improved operation. The heats were more uniform and uncertainty as to results of furnace output was largely eliminated.

Referring again to the diagram of a furnace, the gas checker temperature control is obtained by the use of the damper between the air and gas valves. When this damper is lowered a smaller proportion of the waste gases naturally passes through the gas checkers thus cooling them off; within reasonable limits the adjustment of this damper will give any desired temperature.

In doing this, however, great care must be exercised to see that the air flues and air valve are of ample capacity to take care of the increased volume of waste gases, for if they are not, furnace stagnation results when any attempt is made to lower gas checker temperature and thus defeats the attempt to improve the furnace operation.

Air Valves Reference has been made to sizes of air valves and again let it be said that air valves are frequently if not generally undersized; not so much for the air entering as for the waste gases leaving the furnace.

The usual type of air valve with its sharp turns and restricted passageways imposes a marked resistance to the free flow of the waste gases; the significance of this resistance is not generally recognized. In a number of instances it has been found that the resistances of valves of supposedly ample size was over 50% of the stack draft. In one case a furnace gave considerable trouble because of faulty draft. On this account a much taller stack was built at considerable expense but the change made little difference in the operation of the furnace. It was then found that the loss of draft due to the valve and turns leading to and from it amounted to 72% of the stack draft. A larger valve overcame the difficulty.

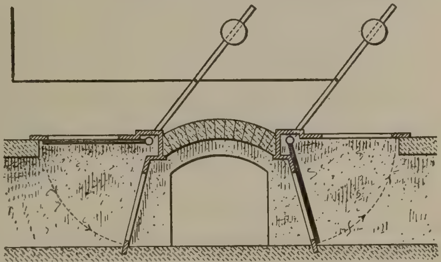

FIG. 4.

A valve with straight line flow in which the sharp turns and bends are eliminated offers the least resistance to furnace gases. In fact, its resistance is practically nothing and with such a valve the gas checker temperatures are more readily controlled without danger of furnace stagnation. A valve of this type (Fig. 4) installed on a tube welding furnace made a marked improvement in the operation of the furnace and permitted full range of gas checker temperature regulation with no indication of furnace stagnation.

SIMPLEX ENGINEERING CO.
WASHINGTON, PA.

BRICK AT LESS COST[1]

By W. D. Richardson

ABSTRACT

Lowering cost of making brick should increase their use. This is a function of the American Ceramic Society. Drying brick in kiln is practical and economical. Adapted to clays that stand rapid drying and for common brick, paving brick and stiff-mud fire brick. History of kiln-drying system. Open-top continuous compartment kiln best adapted for system. Description of system in plant at New Hope, Pa. Saving in labor, damage to brick on cars and in deterioration of cars. More compact plant, all under roof.

To make good brick at less cost, wherever possible, is a business duty and a public benefaction. Reducing the cost of production should not only increase the profits of the manufacturer, but should also lower the selling price to the consumer.

In a recent number of the *British Clayworker* a writer says: "It is often much easier to save £50 in the works than to land an order which will net half that amount, because in the first case the figuring is against a certain figure which was estimated to yield a profit with ordinary methods, while the getting of an order is more speculative. Consequently, time spent in devising handling methods that will save money over the original estimate is always profitable."

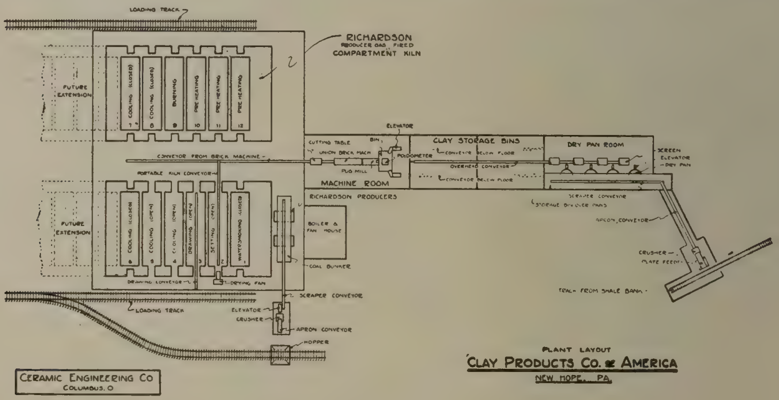

Fig. 1.

In 1906, my attention was called to a "system" that eliminated the drier. The brick were conveyed on the off-bearing belt directly from the cutting table to the kiln, where they were set and dried in superimposed layers. This was at Knoxville, Tenn. The "system" was patented by Alexander Scott. I had a hand in the designing of five plants for this system, three of them new plants and two of them old plants remodeled.

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[1] Presented at Atlantic City Meeting, Feb., 1924 (Heavy Clay Products Division).

Four of these plants have been in constant operation since then, producing common stiff-mud brick at low cost. Believing that this system had large possibilities of improvement, I took up the study of it again about three years ago.

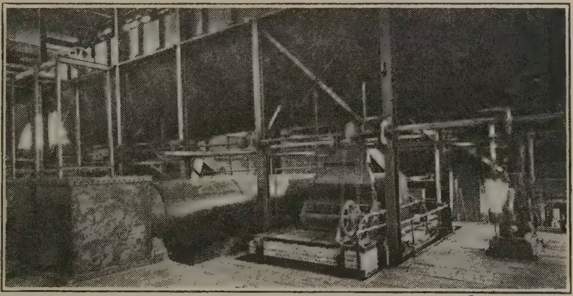

FIG. 2.—Coal bunker over producers.

The problem then, and upon which the success of the system in the largest way depended, was the designing of a kiln that was equally well adapted for the setting, drying and firing of the brick. Such a kiln should meet the following requirements:

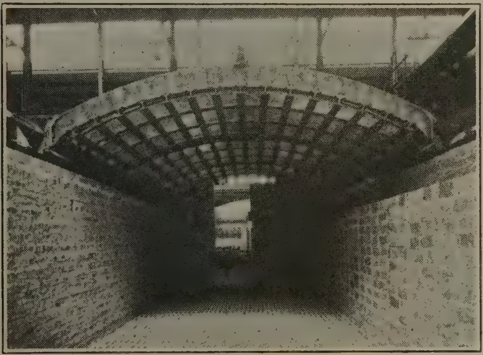

FIG. 3.—Cast iron frame of portable crown.

1. The kilns should be close together, so that the main conveyor may be as short as possible.

2. The kiln should be updraft for drying and down-draft for firing, and be efficient in both operations.

3. The kiln should be open-top, with a portable covering over the setting, or should have a more substantial portable crown, depending upon the size of the plant and the amount of money to be invested.

4. The kiln should be fired automatically with fine coal from the top or with producer gas from the bottom.

5. To meet these conditions and be economical in fuel and labor, the kiln must be continuous and fully regenerative.

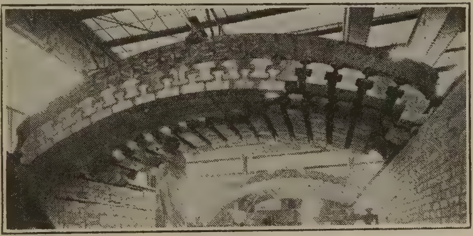

FIG. 4.—Method of supporting refractories on iron frame of portable crown.

It is only in recent years we have learned how to build a kiln that would meet these requirements. This has been a gradual development and not the work of any one man.

The practical generation and application of producer gas made possible a compartment kiln of more rapid firing, more uniform distribution of heat, better control, higher temperatures and a cleaner, better product than had been possible. Such a kiln had been in use in Europe for forty years or more, and three or four of these European kilns had been built in this country for the burning of fire brick. These designs were not well adapted to American conditions, at least at that time, when the price of coal was very low. Some years later, Youngren designed and built a number of continuous compartment kilns for producer-gas firing, some of which are in successful operation today.

In 1915, I made improvements on the producer-gas-fired continuous kiln, and in 1916 designed a compartment kiln for the automatic firing of fine coal. In the past three years I have also developed these kilns so that freshly-made brick can be successfully dried in them, without interfering with firing in the usual manner.

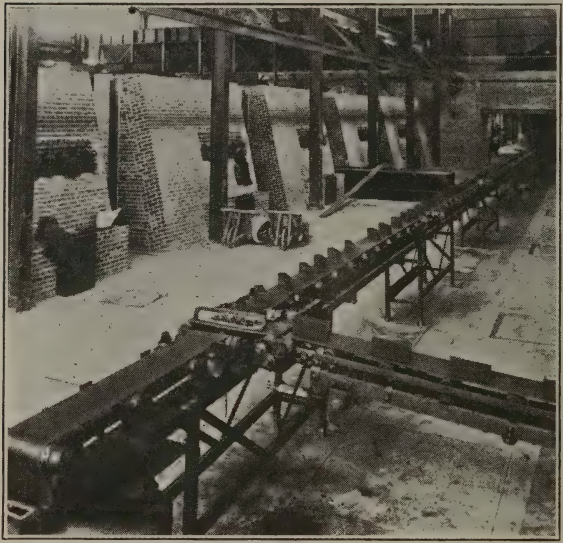

Fig. 5.—View of kiln and automatic conveyor.

In 1902, J. Parker B. Fiske[1] built a continuous compartment kiln with a portable crown. The portable crown on this kiln neither gave trouble in operation nor required repairing. Portable crowns permit hastening the last stages of the cooling, make more comfortable and sanitary conditions for the workmen and, what is most important for the kiln-drying system, permit the top layer of brick to be set without inconvenience.

The traveling crane for moving the crown sections makes possible laying up the door casings quickly in two units. This not only saves labor, but does away with the nuisance of tearing down casings and piling the brick near the door where they are always in the way and make an unsightly litter.

Scott's scheme consisted of a conveyor from cutting table to kiln, a main conveyor running parallel with the row of kilns, and a portable branch conveyor from this main conveyor through the kiln. The branch conveyor was operated from the main conveyor, but required the constant service of a man to transfer 50,000 bricks a day by hand from the main conveyor to the kiln conveyor. At the Builders Brick Co., Chicago, where this system is putting into the kiln about 200,000 bricks a day, there are three branch conveyors from the main conveyor into the large up-draft kiln. Two of these conveyors have automatic switching devices, but to one conveyor the brick must be switched by hand. Their automatic switching device rounds somewhat one corner of the brick.

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[1] "The Elimination of Hand Labor in Brick Making," *Trans. Amer. Ceram. Soc.*, **5,** 21–49 (1903).

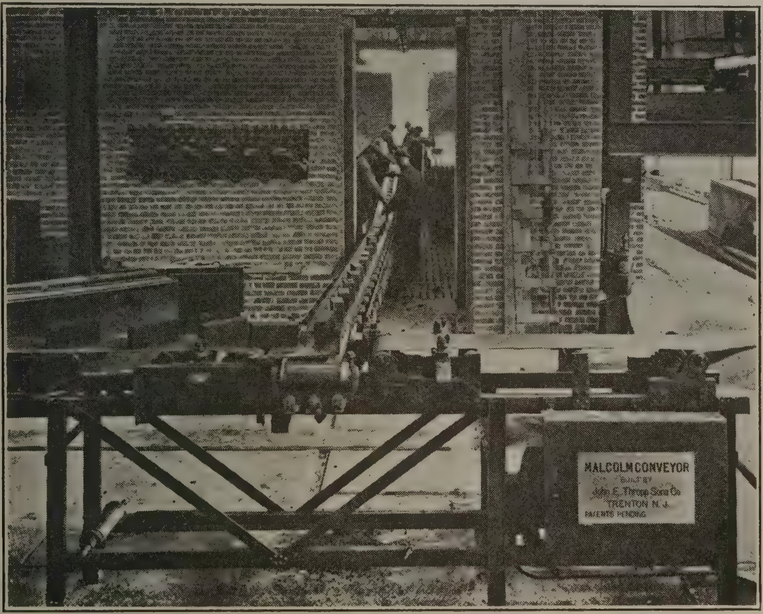


Fig. 6.—Setting brick direct from cutting table.

At New Hope, Pa., where side-cut brick are made, William Malcolm is successfully switching brick automatically from the main conveyor to the portable kiln conveyor without damaging the corners of the brick.

Brick can be dried in the kiln successfully, with the heat from cooling compartments. A layer of brick 12 courses high (50,000 bricks) is set over the floor of the kilns from the conveyor. For the next day's setting the conveyor is then raised to the next level.

The central draft-collecting flue of each compartment extends back into the doorway, with an opening in top at end of flue. As soon as the 12-course layer of brick has been set in a compartment, a sheet iron breeching is used to connect the central draft flue in a cooling compartment with an underground heat-supply duct with openings in top opposite each compartment. A portable fan is connected with this outside duct discharging into the central draft flue of the compartment in which bricks are set for drying. The heat, distributed through the cross flues, is blown up through the layers of brick. Some time before the factory starts the next morning, the drying fan is stopped, the brick being either thoroughly dry or dry enough to support another layer of 12 courses on top of them. The second layer of 12 courses completes the setting of the compartment and the kiln conveyor is moved by the traveling crane to the next compartment which has just been emptied. The crane then picks up the door casings from the cooling compartment and places them in the compartment that has just been filled.

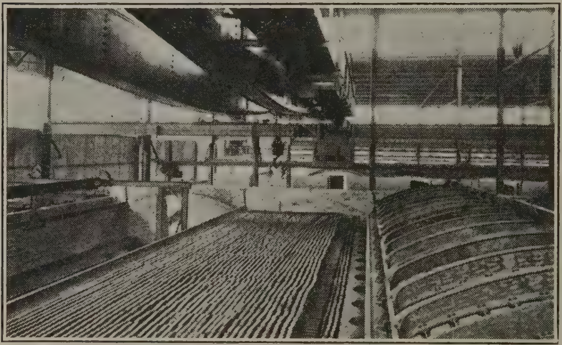


Fig. 7.—Top view of kiln. Chamber on extreme left is empty. Center chamber has just been set. Chamber on right has portable crown in place. Traveling crane above.

The upper layers of brick are then dried in the same manner as were the lower layers. When the drying has been completed, the crown sections are taken from a nearly cooled kiln and placed upon this kiln just dried. The draft connection is moved forward to this compartment, so that the hot gases from the kiln under fire will be pulled over into this compartment in the usual manner of continuous kiln operation.

Ordinarily the making of 50,000 stiff-mud bricks a day requires at least four men to take the brick from the off-bearing belt and place them on the drier cars: one man to transfer the cars to the drier, and one man to transfer the cars to the kiln. Ordinarily it takes at least four men to set the brick from the cars into the kiln. So, figuring the daily wages of these ten men at $5 the cost of handling the brick by the usual method would be $50 or $1 per M brick.

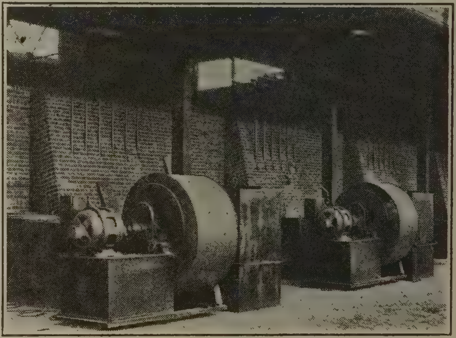


Fig. 8.—Drying fans.

By the kiln drying system the brick are not touched until they get into the kiln where six men take them from the belt and set them. This is a saving of $20 a day or $.40 per M brick. In addition to this saving of labor, there is the saving of the up-keep of the drier cars and the damage to brick while being transported on the cars through the drier and to the kilns. Also, the waste heat for drying is taken only a short distance, never more than 50 feet, from the cooling kiln to the kiln being dried, which means less loss of heat and less power for operating fan. There are other smaller economies.

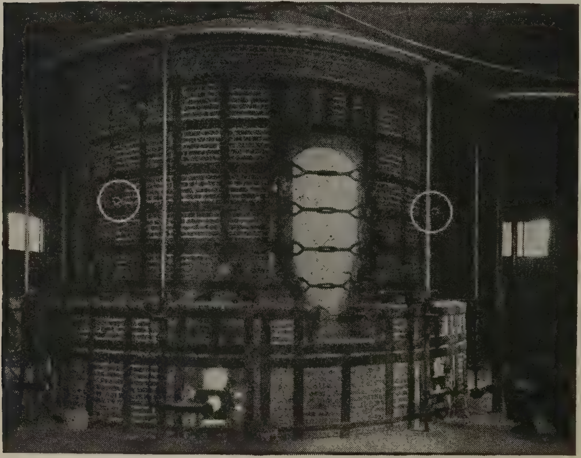
The system can be adapted to the soft-mud as well as to the stiff-mud process. It is a practical and economical method of making common brick, paving brick and stiff-mud fire brick. In some cases it is also practical for face brick. The continuous compartment kiln makes a compact plant, all under cover: a brick factory instead of a brickyard. Whether fired with coal or producer gas, the coal is unloaded from railroad cars automatically, elevated and stored in bunkers at end of kiln. The feeding of the coal is automatic, so that the burner can give his whole attention to the regulation of the fires. His qualifications can be mental, rather than physical. Moreover, the firing of such a kiln can be reduced to a system and uniform, positive results be assured.

Ceramic Engineering Co.
Columbus, Ohio

PYROMETRY—PAST AND PRESENT[1]

By R. P. Brown

Quite a number of years ago, I read a paper on pyrometry before the American Ceramic Society, when pyrometers for burning clay products were comparatively little known. Today it is not necessary to explain what a pyrometer is, for during the past ten or fifteen years, pyrometers have been generally adopted by the more progressive plants. Of course, there are many small and non-progressive plants which are firing their kilns without pyrometers, but today these plants are becoming the exception rather than the rule. From my experience, it would be a safe guess that over 60% of the kilns in which brick, terra cotta, drain tile, sewer pipe and refractories are burned, are equipped with pyrometers, whereas 15 years ago, not 5% of the kilns were equipped with pyrometers.



A pyrometer equipped oil-fired porcelain kiln. Thermocouples shown in "rings".

What has warranted such a general adoption of pyrometers during the past fifteen years and just what results have been obtained by their use?
I can suggest the following:

1. To save fuel.
2. To decrease burn overs.
3. To reduce breakage loss.
4. To afford a check on the burners.
5. To obtain maximum efficiency generally in kiln firing.

While undoubtedly in many plants, marked savings have resulted from the installation of pyrometers, this depended entirely on the efficiency in kiln firing, prior to the installation of the pyrometers. Some plants have reported 15 to 20% saving in fuel whereas others had comparatively little saving. I know where pyrometers were considered of no benefit because no marked saving resulted immediately after their installation. I even know some who assumed that in some remarkable manner, the pyrometers themselves would reduce fuel consumption and automatically fire the kilns. Pyrometers are nothing more than a good tool: an aid in obtaining the desired results.

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[1] Presented at the Atlantic City Meeting, Feb., 1924 (Refractories Division).

Some plants are fortunate in that the kilns are efficiently fired even without pyrometers. But, let us take a case where the head burner had been firing for thirty years and his eye was still excellent: no marked saving could result from installation of pyrometers. But suppose this head burner can no longer fire the kilns, and records had been secured of the desired temperature at each hour of the burn, which enabled the fireman to operate by pyrometers. Imagine the feeling of relief on the part of the manager when he realized that he had pyrometer records on successful firings, that his plant knew how to fire the kilns by pyrometers and they were not "lost" because the head burner was no longer in charge. The pyrometers in this case were good insurance.

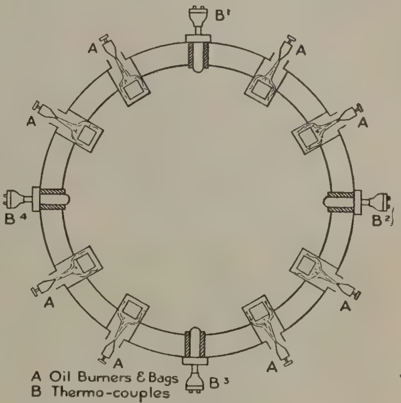
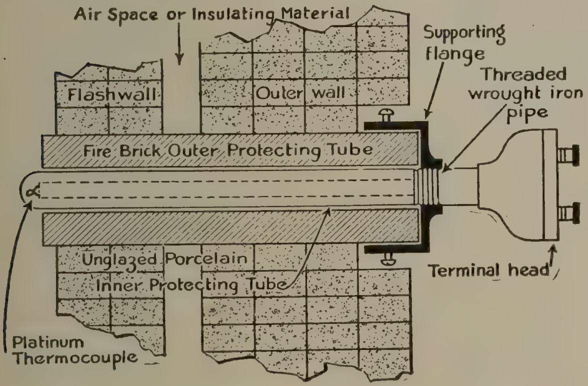


Diagram of oil burners and bags and thermocouples as installed in the pottery kiln shown here. The thermocouples are wired to the Indicating Pyrometer to switchpoints marked B-1, B-2, B-3, B-4, respectively. This identifies them to the worker and shows which oil burners (if any) need regulation.


Air Space or Insulating Material
Flashwall
Outer wall
Supporting flange
Threaded wrought iron pipe
Fire Brick Outer Protecting Tube
Unglazed Porcelain Inner Protecting Tube
Terminal head
Platinum Thermocouple

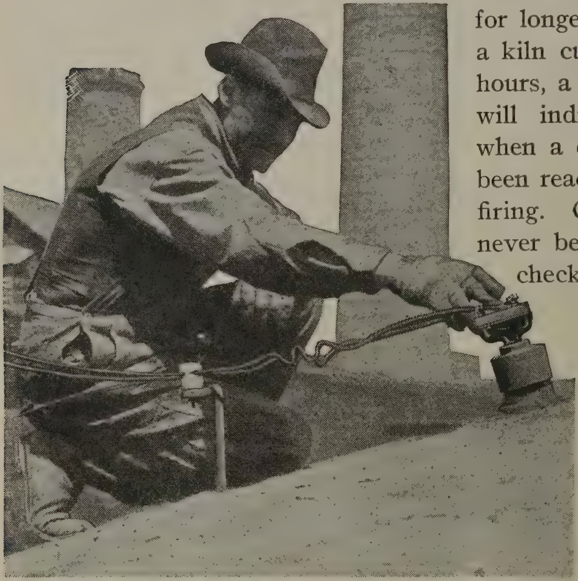
Details of thermocouple installation on pottery kiln: The 22″ open-end fire-brick tube extends completely through the kiln wall, slightly beyond the inner side of flash wall, and the porcelain protecting tube extends into the kiln a few inches beyond the fire-brick tube. The thermocouple wire is of platinum-platinum rhodium, as this metal most successfully withstands high temperatures.

Pyrometers are just as much a necessity in the modern plant as fire insurance. The plant is protected against lost time and poor ware.

The following types of pyrometers were introduced in ceramic plants in the order named:

1. Seger cones.
2. Expansion pyrometers.
3. Thermo-electric pyrometers.
4. Radiation pyrometers.
5. Optical pyrometers.

Seger cones measure heat treatment. They are affected by both time and temperature; they do not measure temperature. The temperature scale given for the various numbered cones was obtained in a small furnace in a few hours and does not hold for longer lengths of firings. If a kiln customarily is fired 100 hours, a certain numbered cone will indicate quite accurately when a certain temperature has been reached after 100 hours of firing. Cones, however, must never be used with the idea of checking pyrometers as they are not strictly a measure of temperature.


Thermocouple installed through crown of brick-kiln. Wiring supported by bracket and insulators.

Cones are not satisactory for comparison fof firings of varying lengths of time. They do not indicate or record the temperature throughout the entire burn. The temperature might have dropped off before or after the cone softened with no record obtainable by means of cones. Cones, therefore, can be used only to indicate when a kiln has obtained a certain temperature after a certain length of time and are limited entirely to that information.

Expansion Pyrometers These instruments have been used for some thirty or forty years in ceramic plants. The instrument works on the principle of the difference in expansion of a steel tube, inside of which there is a non-expanding graphite or porcelain rod. The difference in expansion is indicated in degrees of temperature. This type of instrument can be used satisfactorily throughout the water-smoking period, and up to 1400°F (760°C). The balance of the burn must be carried on without the aid of an expansion pyrometer.

Thermo-Electric Pyrometers It was not until the advent of the thermoelectric pyrometer that pyrometers were adopted to any extent in ceramic plants. The first thermoelectric pyrometers were imported from Europe about 1900. They have been manufactured in this country since 1905. The adoption of thermo-electric pyrometers in the ceramic industry has occurred, therefore, within the past 18 years.

In periodic kilns, we can use thermocouples formed of wire of base metals such as nickel-chromium and nickel which have a high melting point and good heat-resisting qualities. If we properly protect such wires from contamination of gases, our experience indicates that in periodic kilns, this type of thermocouple is satisfactory for temperatures up to 2200°F or 1200°C. For protecting the wires, it is good practice to use a porcelain tube which is impervious to gases and an outer heavy tube of fire clay or silica to afford mechanical protection to the porcelain tube.

An alternative satisfactory method is to protect the nickel-chromium wires with a pure nickel tube. We have found this method quite satisfactory for temperatures to 2200°F (1200°C).

If the thermocouples are to be used in a continuous kiln where chambers or sections operate constantly at a certain temperature, the use of the nickel-chromium thermocouple should be limited to 1800°F (1000°C). We have in this case an entirely different condition. A thermocouple may withstand 2200°F (1200°C) for 24 hours twice a month in a periodic kiln, but it will not stand this temperature day in and day out in a continuous kiln. This point is not sufficiently considered in the selecting of the proper thermocouples to use for each application.

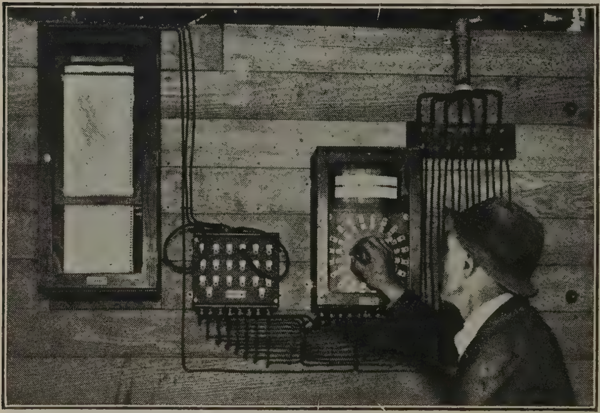
Platinum thermocouples should be used for higher temperatures. For temperatures between 2200° and 2600°F in periodic kilns, platinum thermocouples, when properly protected, give very satisfactory results. For continuous kilns, platinum thermocouples are desirable for all temperatures between 1800°F (1000°C) and 2600°F (1430°C).

Indicating pyrometer, equipped with 8-point switch, for reading the temperatures of eight thermocouples. Each point bears a number corresponding to the number of the thermocouple, so that the thermocouple is readily identified.

Platinum thermocouples must never be protected with metal tubes. It is essential that platinum thermocouples should always be protected by impervious tubes of porcelain or silica. Glazed porcelain tubes are available for temperatures up to 2300°F (1250°C), and vitrified porcelain tubes for all temperatures above this for which a platinum couple can be used.

Radiation Pyrometers

The radiation pyrometer is a thermo-electric pyrometer with the thermocouple located back in a tube. Instead of inserting the thermocouple directly in the kiln, the thermocouple is placed outside the kiln and is heated by radiation. This method is of advantage in that the thermocouple will not be destroyed by the high temperature but certain variables enter in which may result in erroneous readings. For example, it is necessary to have what is called "black body conditions" to obtain correct readings. Black body conditions can be obtained if the radiation pyrometer is focused on a closed end fire-brick tube, projecting inside the kiln.



Indicating pyrometer with 20-point switch mounted alongside a duplex (double chart) continuous recording pyrometer. By means of the plug-type switch (center) any two thermocouples can be connected to the recorder and the temperature at any two points recorded.

Radiation pyrometers also have a mirror which may become tarnished in time and the tube may be at too great a distance from the heated body and erroneous readings result.

There is a field for radiation pyrometers but there are certain inherent objections to this type of instrument which must be overcome before radiation pyrometers are extensively adopted.

Optical Pyrometers

In the common form of optical pyrometer, an incandescent lamp filament is compared with the heated body, the temperature of which is to be measured.

The optical pyrometer may be used for measuring the highest temperatures. It is not necessary to insert any part of the instrument in the kiln. The disadvantage of optical pyrometers is the fact that it is not recording. One has to observe the temperature of the heated body with the eye and adjust the lamp filament to correspond. Furthermore, the instrument requires manual operation and careful handling. The lamps are not interchangeable and it is necessary to determine the readings on the meter in milliamperes, and on a suitable chart, transpose the readings to temperature degrees. There is danger of mistake or error in transposing the readings and the manipulation of the instrument is not easy for the ordinary kiln fireman. While efforts are being made to eliminate some of these defects, the optical pyrometer of today should be used only for portable checking purposes and particularly for temperatures above 2500°F (1375°C).

Pyrometer manufacturers have endeavored to develop their instruments to best meet the requirements of the ceramic industry. I think we might safely assume within the next five years that the kiln at that time which is not equipped with pyrometers, will be a curiosity. Pyrometers unquestionably have come to stay. They have made the lot of the manager or superintendent of a ceramic plant much more pleasant and they are going to be even more essential in the future.

Wayne Junction
Philadelphia, Pa.

OPERATION DATA ON CONTINUOUS DECORATING KILN AT MT. CLEMENS POTTERY COMPANY[1]

By John T. Jans

A continuous decorating tunnel kiln has been in operation since April, 1922 at the Mt. Clemens Pottery Co. After the initial four months which were given over to the running of tests and experiments which resulted in radical changes of the original installation, the kiln has been operating very successfully.

The kiln has a capacity of over 3,000 dozen of semi-porcelain dinnerware for a 24-hour day, and operates continuously, or intermittently if necessary.[2] The kiln is 125 feet in length with a double combustion chamber near the middle with gas flues leading toward the charging end, and then through an overhead flue into the stack.

The ware passing through the tunnel is protected from the direct action of the flue gases by a carborundum muffle. A pressure condition is maintained throughout the kiln. Cooling air is forced in at the discharging end, and gradually heated until it passes the combustion chambers, and from there to the charging end where it is withdrawn. It circulates through the ware heating it by convection.

Fig. 1.

The ware is stacked in bungs on interlocking cast iron cars, each with three shelves 20 x 40 inches. The cars are pushed into the kiln at a uniform rate of from 4 to 5 inches per minute.

Cast iron sand seals in the kiln and on the cars prevent escape of air with resultant waste of heat. The car bottoms are filled with insulating cement.

Transfer cars on each end of the kiln deliver to the charging end and receive at the discharging end. These cars move to a return track running parallel to the kiln. The finished ware is removed from the cars while they are on the return track and periodically the empty cars are moved on by an air cylinder toward the charging end of the kiln where they are reloaded and once more sent into the kiln.

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[1] Presented at Atlantic City Meeting, February, 1924 (Whitewares Division).

[2] High-grade vitrified china in decalcomania and hand-painted effects from the Shenango Pottery Company of New Castle, Pa., and the Onondaga Pottery Company of Syracuse, N. Y., have been sent through the Mt. Clemens kiln with wonderful results.

All of the pushers are operated by air cylinders from a central control table with the exception of the kiln-charging pusher which is an oil-gear pusher.

Steel vestibules at the two ends of the kiln prevent the escape of air while cars are entering and leaving the kiln.

The kiln itself is constructed of fire brick and insulating brick within a steel shell. The weight of the cars is carried by floor beams through the buckstays to the floor. The height of rail is 16 inches above the floor, convenient for loading and unloading ware.

Figure 1 shows the charging end of the kiln with the operator at the control levers. The transfer car is in position in the vestibule and a car of ware is entering the kiln. This view also shows the main kiln pusher which forces the line of cars through the kiln and the air compressor and motor which are the source of power for the other seven pushers. The loaded cars of ware not yet fired are shown on the return track.

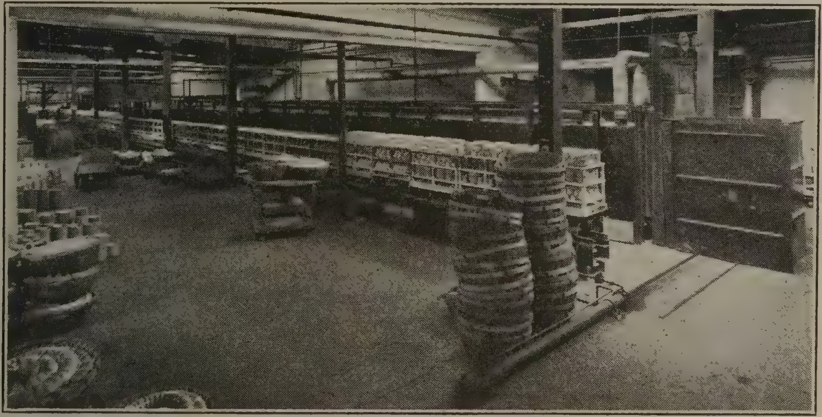

Fig. 2.

The discharging end of the kiln is shown in Fig. 2. This view shows several cars, which have just come out of the kiln, then farther to the left a number which have been unloaded and in the distance, the reloaded cars awaiting their turn to be put into the kiln again. The transfer cylinder which moves the transfer car between the return track and the vestibule of the kiln is shown in the immediate foreground.

Figure 3 shows the ware cars in the tunnel with the carborundum muffle tile walls on either side. Note the drop arches overhead and the baffle piers along the side. The sand seal is also shown.

The empty ware cars are shown in the foreground (Fig. 4) on the return track. Note how they are interlocked. In the background is one of the fire boxes with the oil and air piping to the burner.

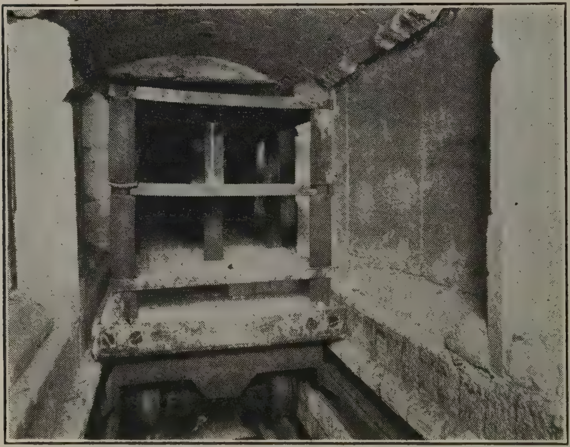

FIG. 3.

Fixed pyrometer couples along the hot zone lead to a recording pyrometer and give an accurate check on the heat at all times. Two of these are equidistant from the center-line of the kiln, one at each combustion chamber in the ware tunnel, showing the operator at once if either burner is too hot or not hot enough.

The oil is supplied to the burners at 50 to 55 lbs. pressure. The low-pressure air for the burners is preheated by passing through a duct directly over the fire-brick kiln arch on the cooling end. This gives a constant supply of air at 150° to 200° for fuel combustion.

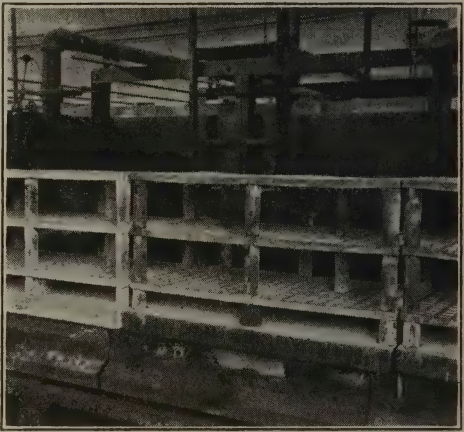

FIG. 4.

The most important advantages of this tunnel kiln are:

1. Economy of and independence of labor as unskilled help can be used on all operations of the kiln. The operating crew consists of one man firing and operating the cars (an intelligent laborer soon masters this), two men loading the cars and a boy to unload the ware.

2. Fuel economy is at least 80%, thereby making the kiln a paying investment from this saving alone. This kiln regularly produces 3,000 dozen of ware with a consumption of 200 gallons of oil. The periodic kilns which this kiln replaced required approximately 10 tons of Higrade Elkhorn Gas Lump Coal for this production.

3. Quantity of production in a given time, enabling rapid shipping of orders.

4. Quality of production in both gold and color work that cannot possibly be obtained with periodic kilns.

5. Reduction of losses from "spitting out," dunting or cracking, overfiring or underfiring, burned gold or gold improperly set which rubs off, and destruction or deterioration of gold or colors from stagnant atmosphere in kiln or from presence of sulphur, carbon monoxide or other impure gases.

It gives gold or colors a smoothness and bright, glossy and lustrous appearance that cannot be regularly obtained in periodic kilns.

A second continuous decorating kiln of similar design has recently completed a satisfactory test run at the Homer Laughlin China Company's new plant No. 6 at Newell, W. Va. This kiln has several additional improved features of interest, chief of which are automatic temperature control and hydraulic operation of ware cars throughout, replacing the more or less uneven operation of the air cylinders.

Here the cars are operated from one control station and in addition to the four-point pyrometer there are two L. & N. control instruments which automatically hold the temperature at the hot zone of the kiln at the point at which the ware is to be fired. The variation of the temperature in the ware tunnel is not more than plus or minus 10°F.

This kiln is equipped for firing with either natural gas or fuel oil. The test run indicated a consumption of approximately 1,000 cu. ft. of gas per hour, *i. e.* 120 dozen of ware or about the equivalent of that for oil at Mt. Clemens.

In summary, the advantages claimed for these kilns as a whole are: quantity of production in a given period, quality of production and economy of production not only from a fuel-saving standpoint, but also because of simplicity of operation, enabling unskilled help to be used.

HOLCROFT AND COMPANY
DETROIT, MICH.

WASTE HEAT DRIERS FOR WHITEWARE

By Thomas C. Walker, Jr.[1]

ABSTRACT

This drier is so constructed that the flow of air is transverse to the tunnel. A fan produces a change of air four to six times per minute, drying ten tons of filter-pressed clay in twenty-four hours. The drier may obtain its heat either from the kilns, glass or bisque or steam coils, or the use of both.

Construction

This drier is designed to dry ten tons of filter-pressed cake in twenty-four hours. The tunnel is 33 feet long, 8 feet 6 inches wide, and 6 feet high. A lift roller door is at each end. These doors are very light and also convenient to open and shut. The walls of the drier are built of 4-inch hollow tile, resting on a concrete floor. The top is reënforced concrete, 4 inches in thickness. Hollow tile may be used as a top by using proper reënforcement.

To one side of the drier is a sheet-iron box covering six steam coils. The size and construction of the coils vary with the difference of opinion of various coil manufacturers, and information may be had by sending specifications. From the sheet-iron box there are two sheet-iron ducts, 18 inches square, along the side of the drier. Openings 3 inches by 12 inches, 4 feet apart lead into the tunnel. In the opposite side near the bottom are duplicate ducts, except the size of the openings, which are 6 inches by 12 inches. The exhaust duct leads to a T.

At the top is the exhaust stack having the blast gate "S" (see Fig. 1). At the bottom is the return duct of sewer pipe 18 inches in diameter having the blast gate "R." This gives a complete circulation of the drying air through the fan, drier, and back to the fan again or the drier air may be exhausted through the blast gate "S" and the exhaust stack. It is well that the sheet-iron duct be covered with asbestos to reduce the radiation.

The fan may be of any type having the following requirements: The inlet must be 18 inches or more in diameter. Four ounces or more static pressure must exist. Five thousand to seven thousand cubic feet of air must be delivered per minute. Leading to the inlet of the fan is a 24-inch sewer pipe having the blast gate "K" which connects the kilns to the fan. If the length of the duct needs to be more than 150 feet a larger sewer pipe is required, for a larger waste heat duct will reduce the frictional resistance of the air. From actual experience an 18-inch duct more than 100 feet long is insufficient for a fan of this type.

The frames of the cars are 26 inches by 48 inches made of 5-inch channel iron. Inside of the frames at the center are two cast-iron wheels and at

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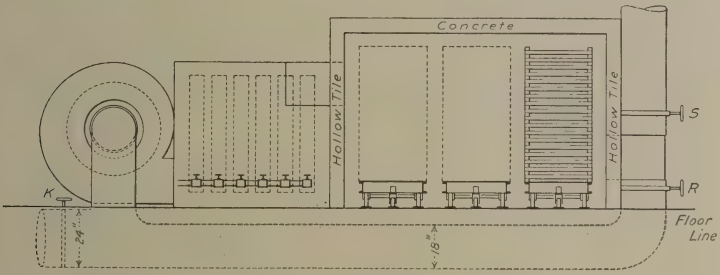
[1] Recd. Feb. 15, 1924.

each end is a 6-inch caster wheel to keep the car in a horizontal position, also to facilitate the changing of direction. This arrangement makes it possible to move the car about with ease.

On the drier floor are 6-inch band irons used as a track and between the band irons is a 3-inch channel iron serving as a track for the caster wheels, keeping the cars in line and also causing the large wheels to run on the band irons.

No means has been designed for moving the cars through the tunnel. Possibly a winch at the drawing end would be an advantage but in most cases the wet cars are moved by hand at the time the dry cars are drawn.

This type of car is built for filter-press cake. Two cars are placed along side the press and as the cake is removed the pallets of one car are placed on the empty car being filled with filter cake. They are then put into the drier and from the drier to the pulverizer.



END VIEW
Section thru A-A

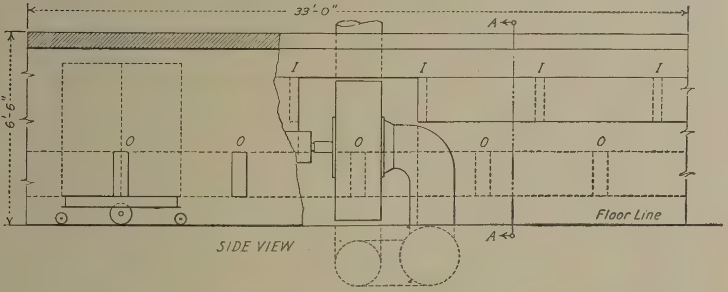


FIG. 1.

By this method the cost of handling is decreased.

The pallets are wooden strips $^7/_8$ by $^3/_4$ inches so constructed when stacked on the cars, to give ample circulation of the heated air between the filter-press cakes. Each pallet is 24 x 26 x 2 $^5/_8$ inches. They are stacked 20 high on a car making a complete load of 40 to 46 cakes. Two or three cakes on top without pallets will dry just as rapidly as those near the center, due to a better circulation of air.

Operation

A drier of this type operated most efficiently between the temperatures 190° and 200°F. Let us suppose that we have one or more cooling kilns: possibly one bisque that has been fired to cone 10 or 12 and has been cooling 8 or 10 hours, and a gloss that has just been fired to cone 1 or 2. These two kilns are turned into the drier through the blast gate "K." To facilitate the operation, a recording hygrometer is attached inside the tunnel near the center, which will give the condition of the drier. The blast gate "K" is open completely, blast gate "R" is shut, and blast gate "S" is open, allowing the waste heat to pass through the drier but not back into the fan. The temperature of the dry bulb after two or three hours will rise to 250°F, giving approximately a relative humidity from 10 to 12%. In this case the relative humidity is very low and may cause cracking of the filter cakes but it does not matter as they go to the pulverizer. Since the humidity is not over 12% the cakes will dry completely at this temperature in twelve hours or even less.

Let us consider the drying after 24 hours. The loaded cars having been put in at intervals, those near the drawing end are nearly dry. The gloss kiln has been taken off because it has been spent of effective waste heat. The dry bulb now reads 160°F and the wet bulb 108°F, giving a humidity from 15 to 17%. One coil or possibly two is turned on to increase the temperature to 200 or 205°F causing the humidity to drop to nearly 12% again. The blast gate "R" is open slightly and "S" may be closed. This will cause an increase in drying even though the humidity may rise slightly. At this temperature and under these conditions the cake will dry in approximately 16 hours.

If the bisque has cooled so that the waste heat is 130°F or under, there will be very little drying. But adding heat through the coils and still using heat from the kilns the drier may be operated so the maximum time of drying is no more than 24 hours. In this case the blast gate "R" should be completely opened as also the blast gate "K." Blast gate "S" should be nearly shut, allowing only a small amount of air to pass into the exhaust stack. The relative humidity will rise to 20 or 25% for the temperature is now about 200°F but the drying will take place very rapidly, due to the circulation of the air through the tunnel, for the air changes every 10 or 15 seconds without consuming a large quantity of heat from the coils.

The Usual Type of Drier In most driers the circulation of air is from end to end. The air generally is fed in at the bottom of the drawing end. The heated air takes up enough moisture to acquire relatively high humidity, thus drying the ware very slowly at the entering end Of course this is a condition ideal for the drying of clay wares. But the car that sets over the hot air duct will be perfectly dry, especially on the bottom, while a few cars back will be nearly as wet as when entering the drier 10 or 12 cars before, because the humidity cannot be controlled. Several driers of this type are being used in wall and floor tile plants and during rush periods have proven insufficient.

In the drier here described the air enters at the side near the top. The inlets "I" are spaced 4 feet apart, each having a blast gate. As the hot air enters the drier it has a cyclonic effect, circulating through every part of the tunnel even to the corners. This makes the clay dry just as rapidly in any part of the drier as it will at the center. Also the flow of air from side to side has less resistance through the clay and a better circulation through the cars and pallets. The blast gates at each inlet allow the flow of air to be changed in the different parts of the drier, drying the clay more quickly at the drawing end if needed or any other part of the drier.

Efficiency in operation of a drier of this type gains by experience. Just how much to open and close the blast gates for the different conditions is difficult to say, but an operator will learn very shortly the best position of each blast gate for each condition.

The temperature should never drop below 180°F and the humidity should never be above 30%.

This drier requires very little attention, for the operation may be handled by the foreman of the department. His attention for a few minutes once or twice a day is sufficient.

Los Angeles Pressed Brick Co.,
Los Angeles, Calif.

THE OXIDATION OF CERAMIC WARES DURING FIRING. V.—A QUANTITATIVE STUDY OF THE NATURE OF SULPHUR EVOLUTION IN KILN-FIRING.[1] (Part I)

By Frederick G. Jackson[2]

ABSTRACT

The absorption and evolution of sulphur gases in four industrial brick kilns were studied. Curves are shown giving the cumulative amounts of sulphur entering and leaving the kilns, and of the kiln content of sulphur. Surfaces and hearts of draw trials are analyzed to show the progressive change in nature of the sulphur compounds in the ware.

Introduction

The preceding work[3] was on a laboratory scale. This paper covers similar investigations under industrial conditions. Several new factors are introduced. In kiln practice, the fuel often puts more sulphur into the kiln than is contained in the green ware. The temperature difference between the top and the bottom of a kiln is frequently sufficient to reverse the direction of a reaction. Considerable water is evolved by the fuel as well as by the ware. Lime absorbs sulphur at one stage of the firing and iron oxide at another. A variety of sulphur compounds are in clays which give off sulphur at different temperatures and rates.[4] Some of these compounds may be native in the clay and some may be formed in the course of the firing.[5]

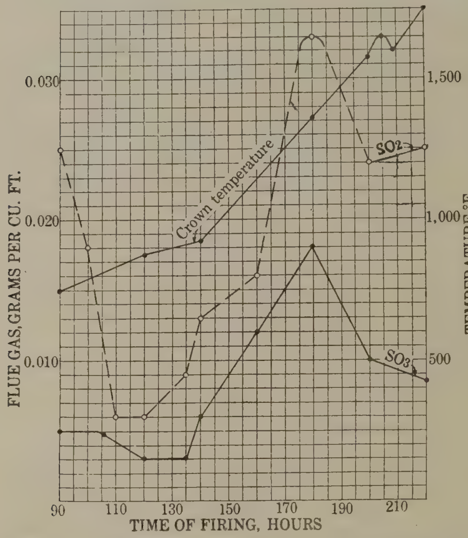


Fig. 1.—Results of tests at a face-brick plant.

The First Industrial Study

The first study was made at a face-brick plant. They use a Lower Kittanning fire clay, to which is added about 5% iron as mill scale. The kilns are coal-fired, round down-draft, each having four stacks in the wall. Each kiln holds about 140 tons of ware, and requires about 45 tons of coal per burn. The sulphur content of the ware was 0.30%, mainly as pyrite. The coal contained 1.8% sulphur, also chiefly pyrite. Thus 840 pounds of sulphur was contained in the ware and 1620 pounds in the coal. All of the latter, except the amount fixed in the coal ash, went through the kiln.

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[1] Published by permission of the Director, U. S. Bureau of Mines.

[2] Associate Chemist, Ceramic Station, Columbus, Ohio.

[3] See "The Decomposition of Various Compounds of Iron with Sulphur under Simulated Kiln Conditions," by Frederick G. Jackson: *Jour. Amer. Ceram. Soc.*, **7** [4–5], 223, 427 (1924).

[4] *Loc. cit.*, **7** [4], 223 (1924).

[5] *Ibid.*, **7** [6], 427 (1924).

Gas samples were taken through a fused silica tube at the damper in one of the stacks, about 4 feet above ground level. This was connected by glass tubing to the customary Gooch crucible with the asbestos matt and potash bulb.[1] These samples were analyzed for sulphur dioxide and sulphur trioxide.

Nine samples were drawn from several different kilns. The temperature, elapsed time of firing and condition of fires were noted. The results show only a qualitative trend because no consideration was taken of such factors as the amount of excess air, or the rate of firing. The curves (Fig. 1) show in grams the amount of SO_3 and SO_2 per cubic foot of flue gas at various times throughout the firing. The crown temperatures are also shown.

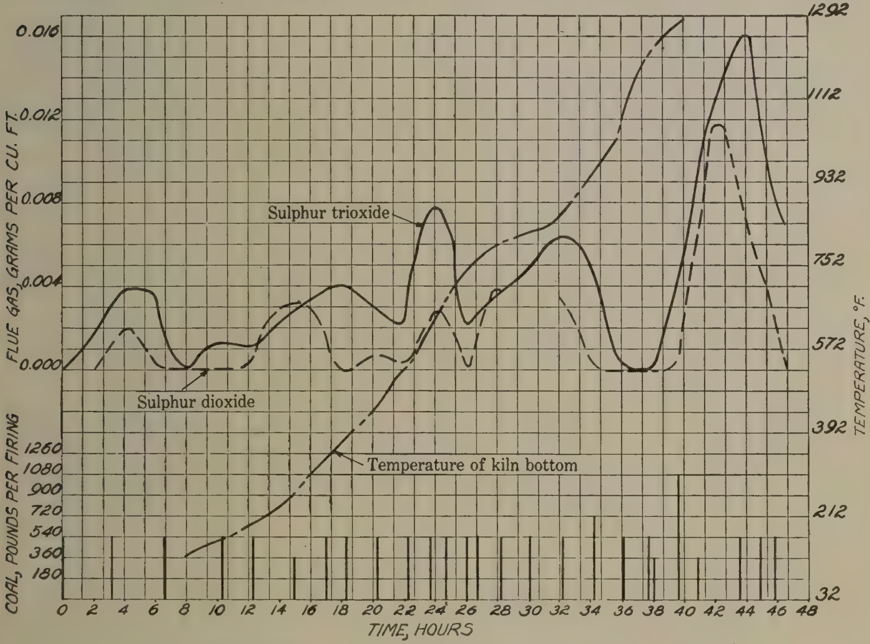

FIG. 2.—Sulphur in kiln burning carbonaceous clay.

Discussion of Results

Evidently there is a great evolution and absorption of SO_2 between the 100th and the 130th hour (770° to 900°F). This then decreases, and a large evolution of SO_3 takes place and continues until the 180th hour (1370°F). Evolution of SO_3 then decreases, while evolution of SO_2 continues at a faster rate than at the early stages of the firing. The latter is probably due to increased firing rate. We thus see two tendencies: first, an absorption of SO_2, and then an evolution of SO_3.

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[1] *Loc. cit.*, **7** [4], 226 (1924).

The Second Industrial Study

This second study was at a plant using carbonaceous clay and on a round down-draft kiln, nearly new, with a single outside stack. The sampling tube was inserted in the stack about 3 feet above ground. A meter reading to thousandths of a cubic foot was connected to an adjustable suction line. Absorption was continuous, the absorbers being changed every two hours. The kiln was set with drain tile, and was fired off in 60 hours. Temperatures were taken at the bottom of the wicket. Results are shown in Fig. 2.

Discussion of Results

Since the percentage of excess air was not measured, these results have only a qualitative value. They show a series of tendencies which will be brought out more clearly in the subsequent quantitative work.

Third Industrial Study: A Pyritic Shale

A more elaborate study was made at a plant where sulphur is a serious problem. The test was carried out on a round down-draft kiln. Red face brick were being made from shale fairly high in pyrite.

The kiln was a 30-foot round down-draft with a large separate stack. The kiln capacity was about 65,000 bricks.

The object was a "sulphur balance," similar to a heat balance. Such a sulphur balance would show the course of sulphur absorption and evolution throughout the firing, and it would give the exact sulphur content of the kiln at all firing stages.

Procedure

To find the percentage of sulphur in the gases entering and leaving the kiln, a tube was inserted at about 4 feet below the spring of the crown where the hot gases had not yet touched the ware. Another tube was set close to the base of the kiln in the main flue leading to the stack. Each tube was extended 2 feet beyond the wall, and into the midst of the gas stream. An analysis of the stack gas was made either just before or just after each test, and the temperature of the kiln was taken both before and after testing.

Samples were taken at intervals of 2, 3, or 4 hours, depending upon the stage of the firing. In order to cover a complete firing cycle, it required from 40 to 60 minutes to draw each sample. In analysis, no distinction was made between sulphur as SO_2 and as SO_3.

A record was kept of the time and amount of coal fired. Samples of coal and ash were taken for analysis.

For every 100 pounds of coal, 67.9 pounds of carbon or 249 pounds of

ANALYSIS OF COAL AND ASH

Constituent	Coal, per cent	Ash, per cent
Carbon	73.3	37.0
Ash	9.1	62.8
Sulphur	1.6	3.4

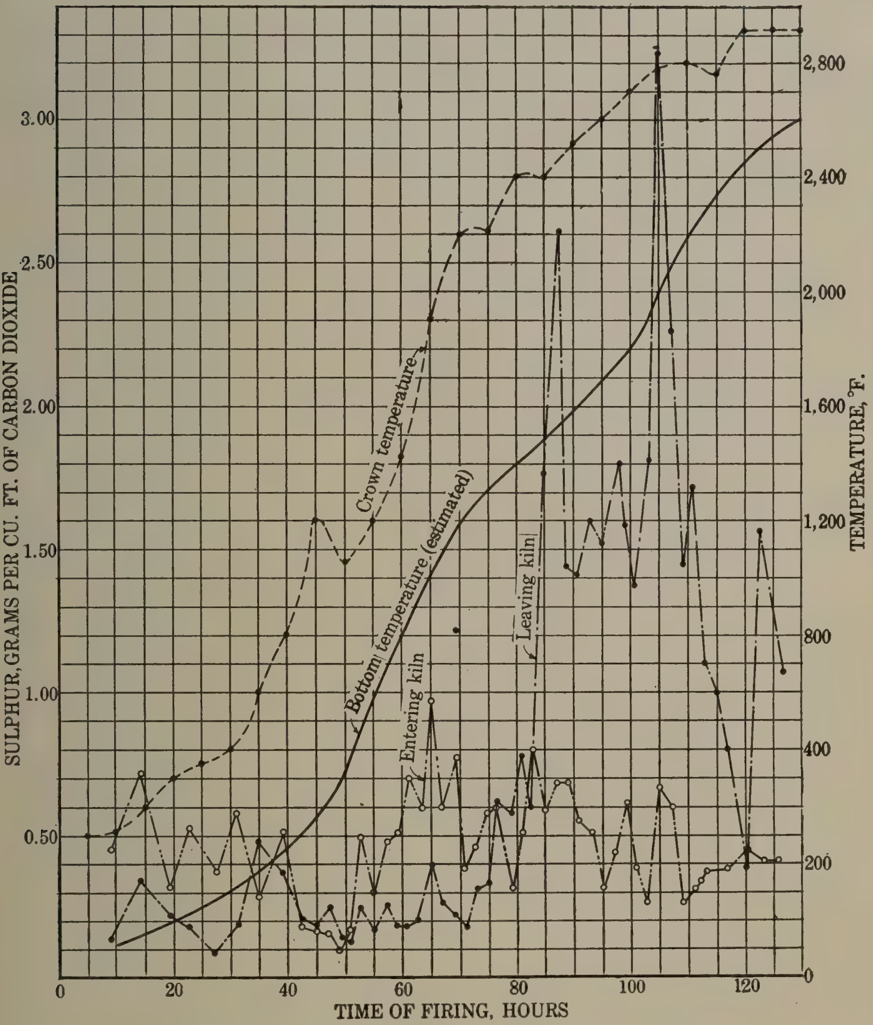

FIG. 3.—Sulphur in pyritic shale.

CO_2 entered the kiln. Under normal conditions of weather this CO_2 would have a volume of 2,532 cubic feet.[1]

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[1] The gases from the kiln were drawn through such a distance of thin glass tubing, as well as through the absorption train, that they were at atmospheric temperature when their volumes were measured.

Calculation of Results The weight in each sample was divided by its volume, giving the weight of sulphur per cubic foot of sample. This weight was again divided by the percentage of CO_2 found in the gas to give weight of sulphur per cubic foot of CO_2. These figures are compared in Fig. 3.

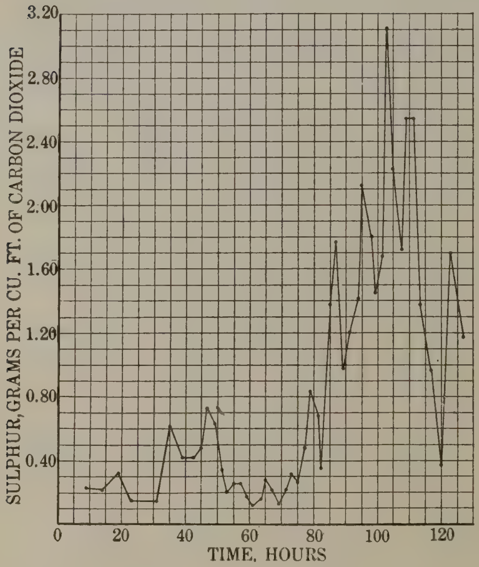

Fig. 4.—Sulphur in pyritic shale recalculated.

The ratio of sulphur gases to CO_2 in the gases entering the kiln each hour should have a constant average throughout the burn, although varying from minute to minute. It was therefore considered more accurate to take the average of 0.46 gram of sulphur per cubic foot of CO_2 and recalculate on this basis. This has been done in Fig. 4.

These figures are rates, not amounts, and take no consideration of the rate of kiln-firing. To take this factor into account, it was necessary to calculate from the firing record the weight (pounds) of coal per hour. From this is calculated the number of cubic feet per hour of CO_2 entering the kiln, and from this the actual weight (pounds) of sulphur both entering and leaving the kiln each hour of firing. The results of these calculations are shown cumulatively in Fig. 5. The general trend of the crown temperature is also shown in this figure.

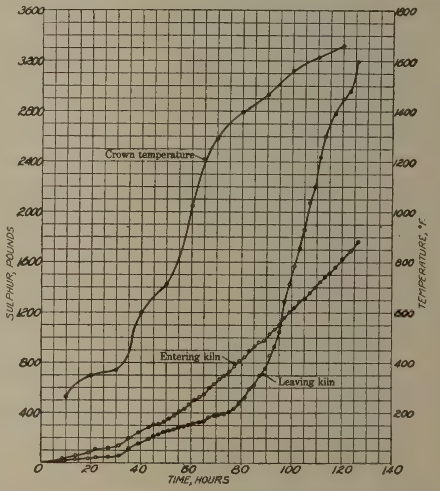

Fig. 5.—Sulphur entering and leaving kiln.

The charge of clay ware consisted of 65,487 bricks, of which 3,900 were "re-sets," and need not be considered. We can therefore consider the charge as being 61,587 green bricks.

It was decided to express all results on a fired-ware basis of 5.4

pounds per brick. The charge then was equivalent to 342,570 pounds of fired ware. Analysis of the green clay showed 0.329% of sulphur on a dry basis, or 0.359% calculated on a fired-ware basis. There were 1230 pounds of sulphur set in the kiln. At the end of 123 hours, 1693 pounds of sulphur had entered the kiln, or 0.494% of the weight of the fired charge. During the same time, 2965 pounds of sulphur, or 0.865% of the fired charge, left the kiln.

Blue smoke disappeared from the stack at the 120th hour.

THE SULPHUR BALANCE

Conditions of sulphur	Weight, lbs.	Per cent of fired brick
Sulphur set in kiln in ware	1230	0.359
Sulphur entering kiln as gases	1693	0.494
Total sulphur entering kiln	2923	0.853
Sulphur leaving kiln in flue gas	2965	0.865
Difference (experimental error)	42	0.012

From these data and from those shown in Fig. 5 a running record is obtained of the actual amount of sulphur in the kiln at all times. This is shown in Fig. 6. Starting with 1230 pounds of sulphur set with the ware, we find that up to the 78th hour more sulphur was entering the kiln than was leaving it. At the 78th hour 338.5 pounds of sulphur had been absorbed in the kiln; then sulphur begins to leave more rapidly than it enters. At 94 hours the kiln contains the same amount of sulphur as before firing. Rapid evolution of sulphur continues until at 123 hours blue smoke has ceased. The evolvable sulphur was out of the kiln.

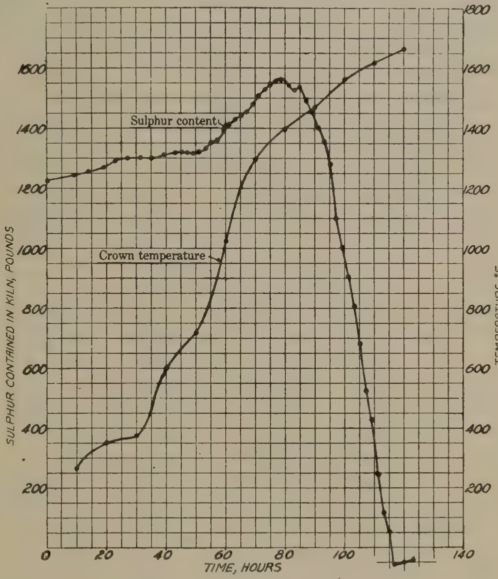

FIG. 6.—Sulphur in kiln.

Analysis of Draw Trials

Draw trials were made at frequent intervals throughout the burn. These were analyzed for sulphur both on the surface and in the center.

Ten grams of each sample were weighed out into a liter beaker and 500 cc. of distilled water added. Each beaker was boiled for 30 minutes, allowed to settle, and then filtered until clear. The filtrate was then heated to boiling, and a little bromine water and a few drops of HCl were added. If still clear, barium chloride solution was slowly added to complete precipitation. The precipitate was then determined in the customary way. This gave the amount of water-soluble sulphur in the sample. Water-soluble sulphur consists of sulphurous and sulphuric acids, some sulphides, sulphites and sulphates.

The residue insoluble in water was next returned to the beaker, and 50 cc. of concentrated HNO_3, 100 cc. of concentrated HCl and 350 cc. of distilled water were added and again boiled 30 minutes. The dilute aqua regia extract thus made was separated, as before, and its sulphur content determined after evaporating most of the excess acid. Pyrite is dissolved by this treatment.

The loss on ignition was determined on a second lot of each sample. The results obtained above were recalculated to a fired-ware basis.

Table I gives the percentage of sulphur (water-soluble and aqua regia-soluble) in both the outer skin and the center of draw trials throughout the firing. The table gives also the approximate temperature to which the brick had been heated.

TABLE I—PER CENT SULPHUR IN DRAW TRIALS, ON BURNED-WARE BASIS

		Outer skin of brick		Center of brick	
Hours burned	Approx. bottom temp., °F	Water-soluble sulphur	Aqua regia-soluble sulphur	Water-soluble sulphur	Aqua regia-soluble sulphur
23	110	0.037	0.308	0.026	0.281
36	185	0.073	0.191	0.048	0.221
51	390	0.236	0.218	0.078	0.277
60	605	0.372	0.011	0.102	0.195
66	725	0.420	0.007	0.144	0.023
72	820	0.449	0.013	0.110	0.154
78	880	0.534	0.011	0.071	0.005
86	950	0.356	0.002	0.249	0.001
92	1000	0.292	...	0.248	...
100	1120	0.352	...	0.233	...
107	1250	0.022	...	0.070	...
111	1340	0.086	...	0.217	...
124	1520	0.038	0.004	0.058	0.004
132	..	0.013	...	0.013	...
142	..	0.021	...	0.012	...
150	..	0.004	...	0.011	...
158	..	0.019	...	0.005	...
165	..	...	...	...	...

Water-Soluble Sulphur

These results give the first quantitative presentation of phenomena that have long been suspected. The amount of water-soluble sulphur, that is, the free acid and the sulphates and sulphites of iron, calcium and possibly other metals, increases greatly on the surface of a brick at the bottom of a kiln. From 0.037% at 23 hours it increases to 0.534% at 78 hours. Figure 5 shows that at 78 hours there was the greatest amount of sulphur (338 pounds) held in the kiln by absorption. The water-soluble sulphur on the surface of the brick then begins to decrease rapidly. The temperature (880 °F) was sufficient to vaporize free acids and begin the decomposition of the solid sulphur-bearing compounds.

The water-soluble sulphur decreases to a very small amount, which is about the same for the inside and the outside of the brick and for the green clay. This is probably $CaSO_4$, which would be unaffected by the temperature attained.

The water-soluble sulphur increased much more slowly in the center of the trials than it did on the surface, nor did it reach as great an amount. A definite core was established by the 51st hour. Samples of this core were green when suspended in boiling water. Sulphur gases penetrated the ware slowly, and increased the water-soluble sulphur gradually. Between the 78th and 86th hours there are two factors which may greatly increase the amount of penetration of these gases: the high concentration of sulphur on the surface and loss of water of constitution. The 78th hour sample lost 5.5% on ignition, and the 86th hour sample lost 2.9%. It may be that the steam evolved made a better medium for transmitting sulphur into the ware than did air. The oxidizing effect of the SO_3 and oxygen which thus penetrated eventually oxidized all of the pyrite and the core disappeared. The reaction was probably somewhat as follows:

$$4FeS_2 + 2Fe_2O_3 + 4SO_3 + 15O_2 = 4Fe_2(SO_4)_3$$

It is evident from the results found in the preceding paper[1] of this series, that $Fe_2(SO_4)_3$ is the principal water-soluble compound formed.

Soon after completion of oxidation of the core, the temperature increased so that the ferric sulphate which had just been formed was again decomposed, and the sulphur content decreased until only $CaSO_4$ was left.

The form of the pyrite in this case was a factor contributing to irregular results. Pyrite occurred as "kidneys" of varying size, and irregular in dissemination. The occurrence of pyrite, as occasional coarse particles, led to its irregular occurrence in the small samples taken for analysis.

Aqua Regia-Soluble Sulphur

Boiling aqua regia will dissolve and convert pyrite into ferric sulphate. It will be seen from the analysis that the pyrite at the surface of the ware began to decompose early in the firing. This was due to the presence of hot sulphuric acid and oxygen. By the 60th hour there was but little pyrite left. Inside of the brick this action took place more slowly. It went practically to completion between the 72nd and 78th hours, when the temperature rose from 820° to 880°F (438° to 470°C). Previous work has already shown that during this temperature range, pyrite tends naturally to lose at least one of its sulphur atoms. When it was established that the pyrite had all decomposed, this aqua-regia extraction was abandoned.

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[1] *Jour. Amer. Ceram. Soc.*, **7** [7], 532 (1924).

Hydrofluoric Acid-Soluble Sulphur Qualitative tests made in some cases showed the presence of sulphur apparently combined in silica complexes or possibly in solid solution, but the technique of a quantitative method of analysis has never been worked out. However, evidence of the formation of sulpho-silicate by this clay was found. An adjacent kiln was being emptied. Close to the tops of the bag walls, where the flame action was greatest, were a few bloated brick. Their surfaces were the proper color, showing that they were not overheated but on breaking them, each showed a large black core full of blebs. Their heating had evidently been too rapid, rather than excessive.

NOTE: Report of other industrial studies and the summary of and conclusions from these studies will be given in the September number of this *Journal.*

GAS AS FUEL FOR VITREOUS ENAMELING[1]

By H. H. Clark

ABSTRACT

The typical furnace described has a burning chamber four feet wide, ten feet long and thirty-four inches high, no muffle being necessary. The furnace is of the intermittent type. All the details of normal production are given together with a résumé of the surprisingly low total cost per hour. A comparison of the average hourly production on 24- and 22-hour bases is given. Also several suggestions are made that will materially effect additional economies in the use of gas for vitreous enameling.

Gas is used for fuel for burning on enamel at the plant of the Cribben & Sexton Company, Chicago, Illinois. The burning chamber in the furnace is 4 feet wide, 10 feet long and 34 inches high, with an effective burning area of 30 square feet. There is no muffle used, as this furnace is of the intermittent type and the gas is off while the ware is in the furnace. Air for combustion is induced at the inspirator, which is of the Surface Combustion tunnel type, operating with a single valve, using gas at 10 lbs. pressure.

The average temperature maintained within the furnace is 1600° to 1650°F and the minimum temperature at which the enamel will mature is 1550°F. The production in square feet for the 24-hour period is 9,216 square feet of 18-gage steel or 9,892 square feet of 20-gage steel, the gage depending on the nature of each day's work. The weight of the burning tools is 156 lbs. and is the weight of tools left in the oven while each load is being burned and removed again to be unloaded. The furnace was in production a total of 22 hours per day. The other two hours were used by the burn-on men to change set-up of pins, and trucking work to and from furnace, and was distributed throughout the 24-hour period, being about 5 minutes each hour.

Production in pounds for 24 hours is 15,013 lbs. of 18-gage steel or 17,311 lbs. of 20-gage steel, there being approximately 4 ounces of enamel on each square foot of ware, which weight is included in the above figures. The weight of the burning tools figured at 156 pounds per load was 59,904 lbs. for the 18-gage stock and 63,648 lbs. for the 20-gage stock. They are investigating the proposition of leaving the supporting tools in the oven, and if this method is practical for their operation, it will reduce the fuel bill.

The production in units per 24 hours was made up of various kinds of ware such as: 14 broiler door panels, 18-gage steel, 18 loads per hour; 72 ash door panels per load, 20-gage steel, 17 loads per hour; 16 oven door linings, 20-gage steel, 20 loads per hour; 27 back guards, 20-gage steel, 18 loads per hour; 22 broiler door panels, 20-gage steel, 20 loads per hour; 5 splashers per load, 18-gage steel, 21 loads per hour; 10 boiler pans per load, 18-gage steel, 16 loads per hour; 12 panels per load, 18-gage steel, 17 loads per hour. On the average for a day, the number of loads per 24 hours was 384 on 18-gage or 408 on 20-gage ware. There were two men per shift and the length of a shift was 8 hours. Manufactured gas was used and the amount of gas used per 24 hours was 39,360 cubic feet, for which the Cribben & Sexton Company paid The People's Gas Light & Coke Co. of Chicago $.72 per 1000 cubic feet. This furnace has been in operation nearly two years and the maintenance has been practically nothing, consisting only in relining a damper, which indicates a long life for the furnace, as from all appearances, it is just as good as new.

---

[1] Written by request for the American Gas Association.

The burning tools used on this furnace are made of chromel and the mechanical lift fork is used. Total cost for burning this coat is as follows:

1640 cu. ft. gas per hr. at $0.72 per 1000 cu. ft.	$1.18
Gas compression expense, including power, water, labor	.10
Maintenance of furnace, compressor and auxiliary equipment	.02
Interests, depreciation, and taxes on furnaces and auxiliary equipment	.14
Total cost per hr. (24 hr. basis)	$1.44

Av. hourly production (sq. ft.
of 18-gage ware enameled)
24-hr. basis—384
22-hr. basis—418

Av. hourly production (sq. ft.
of 20-gage ware enameled)
24-hr. basis—412
22-hr. basis—450

The 24-hr. basis is the average work produced per hour in a 24-hr. period, just as the furnace was operated.

The 22-hr. basis is the amount of work actually produced per hour of production, as the furnace was in operation 24 hrs. per day, but in actual production only 22 hrs. per day.

Av. hourly production (pounds
of 18-gage ware enameled)
24-hr. basis—626 lbs.
22-hr. basis—682 lbs.

Av. cost per 100 sq. ft. of
20-gage ware enameled
24-hr. basis—$0.35
22-hr. basis—$0.32

Av. hourly production (pounds
of 20-gage ware enameled)
24-hr. basis—721 lbs.
22-hr. basis—787 lbs.

Av. cost per 100 lbs. of
18-gage ware enameled
24-hr. basis—$0.23
22-hr. basis—$0.21

Av. cost per 100 sq. ft. of
18-gage ware enameled
24-hr. basis—$0.37
22-hr. basis—$0.34

Av. cost per 100 lbs. of
20-gage ware enameled
24-hr. basis—$0.20
22-hr. basis—$0.18

Several changes are contemplated which will reduce the above costs, one of which is the keeping of the furnace in production for 24 hours instead of 22 hours; by having the work brought to the furnace and taken away by truckers, so that the men burning enamel can devote all of their time to that operation; and arranging the work so as to get longer runs on the same class of ware. Another item is the utilization of waste heat from the furnace which will be used for heating a portion of the drying rooms. Another item is the increased business which this firm expects to do in the coming year, which will result in a lower gas rate, approximately $.64 instead of $.72 per thousand cubic feet.

325 People's Gas Building
Chicago, Ill.

THE DEVELOPMENT OF DECORATIVE PROCESSES AT NEWCOMB

By Mary G. Sheerer

ABSTRACT

The decorative processes at Newcomb are described and the following points emphasized: incising design on wet clay, sponging of surface, biscuit painting and modeling the form by hand.

In speaking of the development of Newcomb Pottery, whether decorative, technical or otherwise, it is well to say first that the pottery was an outcome of the necessity of making a market for the work of the students of the Art School of Newcomb College. New Orleans being so far removed from manufacturing centers, the students of design were unable to get adequate returns for their work after leaving the school.

As an attempt had been made previously to establish a coöperative art pottery, and as it had met with considerable success from the standpoint of interesting the artists and the public, it was decided to push this idea. With the support of the College and the reputation which the Art School had won, it had a backing which the private venture had not.

The object from the start was to make, as soon as possible, a pottery which was professional enough to put before the public and which would reflect credit on the standards of the Art School. With this in mind the work had to be limited in scope, but it had to measure up to professional standards.

The training of the students in the Art School was the backbone of the entire venture and they fell easily and naturally into the decoration of pottery.

The turning, firing and glazing was handled by a potter.

Even in these early days, now about twenty-five years ago, the decorators, as well as the instructor, wanted to experiment with the glazes and the firing, but even the potter had little but empirical knowledge back of him. Mr. Binns'[1] and Mr. Geo. Cox's[2] books were not out and women were not admitted to the school of ceramics at Columbus, Ohio, nor was the summer course in ceramics at Alfred, N. Y., yet started.

The experiments consequently were directed towards methods of decoration.

The instructor made many experiments with slip painting and in laying of clays on a white and red body—resulting in use of the former for some time. A tin cup atomizer, mouth blown, was used, for the backgrounds, with the design painted in slip. It was difficult to keep the slip from drying too quickly in this climate where open windows and breezes are desirable, so this method was abandoned for painting on the biscuit.

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[1] "The Potter's Craft," Charles F. Binns.

[2] "Pottery," George H. Cox.

Large brushes, with plenty of water in the paint, were used on the dry biscuit. Desiring to control the texture of the biscuit we tried the sponging of the pieces before they were biscuited. This led to decorating on the wet clay by incising the design, adding the color on the biscuit. This incising enriched the design, as well as made it more a part of the clay body, and gave opportunity for the desired control of the surface. This method has been perfected by the professional decorators and is still used in the standard ware. The underglaze colors ground in a small pebble mill are mixed with water and a small amount of gum tragacanth in a bowl and applied thin with a brush two or three inches wide. A wash of cobalt oxide of medium tone is put over the entire surface, darker parts are added with a smaller brush, or taken off with an eraser, and green, yellow or pink added. The piece is then dipped in a thin coat of semi-matt glaze and is ready for the final fire.

Newcomb School of Art, New Orleans, La.

The formula for this glaze is as follows:

$$\left.\begin{array}{l}0.103\ K_2O\\0.381\ PbO\\0.516\ CaO\end{array}\right\}\ 0.485\ Al_2O_3\ \left\{\ 1.34\ SiO_2\right.$$

The batch weight of the body:

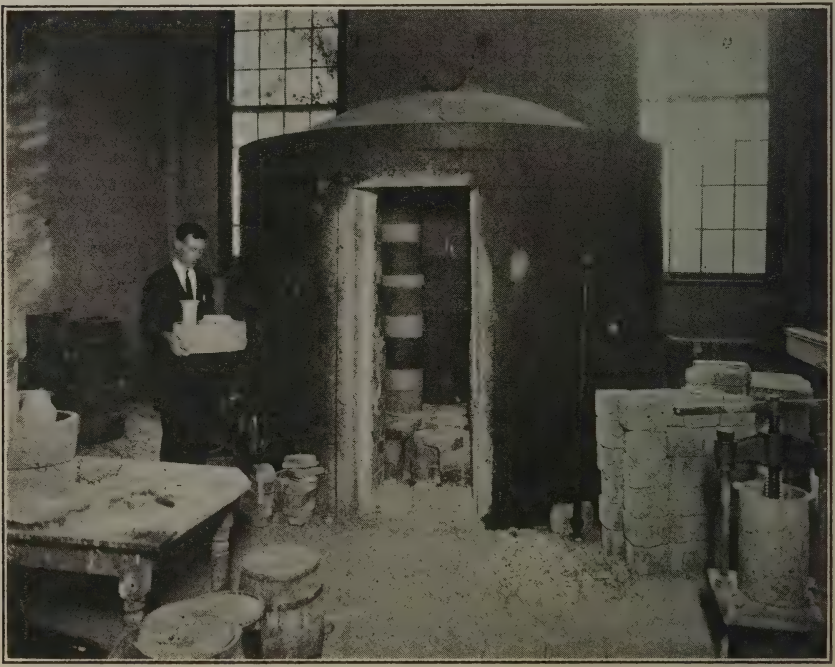
20 Feldspar	35 Covington Clay
10 Flint	35 Ball Clay

The standard ware which has made the reputation of Newcomb Pottery has not only become self-supporting but it makes a handsome return to its decorators. The director of the Art School and of the Pottery has overcome all obstacles in making a success of this first output of the School and has since launched similar ventures in the embroidery, jewelry and bookbinding departments.

Newcomb Pottery, New Orleans, La.

Some years ago, however, a strong urge was felt for still further control not only of the surface but of the form, the glaze and firing—the same impulse so many others were feeling to go deeper into the subject. The fascination of the Indian's method of coiling the pot into form was quickly felt by the students, aided also by their training in form and proportion as well as design—the making and application of glazes was taken up and a revelation kiln and a ball mill installed.

The form and glaze are emphasized in the hand-built pottery, and the decoration, if any, is more in the form of modeled handles, knobs and feet bringing out the plastic quality of the clay, and in working for variety and interest in the quality of the glaze. As building by hand is a slow process, the successfully modeled piece is molded and the forms repeated a few times, each one being finished again and probably variations made of it by further modeling. The clay we have is rather soft and difficult to use, but as it fires hard at the desired temperature and its texture and color are good we had to find a way to keep it from cracking and squatting.



Newcomb Pottery, New Orleans, La.

After making a drawing of a form, we make a circle on paper of the diameter of the base with a soft pencil—place a thick lump of clay, stiffer than that used for coiling, on the circle, and press the clay down evenly with a plaster setter. The drier clay and the greater density caused by pressure of the setter, make for strength and less shrinkage so that we almost never have a crack in the bottom. The coiling of the walls is done in about the usual way, making the walls rather heavy to allow for stretching, and perfecting the modeling with the fingers, which preserves the individual touch and the plastic quality, rather than using the wooden and steel tools which tend to stiffen the form, making it more mechanical looking.

As we do not use the air brush, glazes are superimposed on one another to get variety and depth of effect. The body of the hand-built pottery is the same as that of the standard ware. The various colored glazes are based on the following:

White Lead	167.70	White Lead	129.00
Whiting	25.00	Whiting	50.00
Zinc Oxide	8.10	Raw Clay	90.00
Raw Clay	38.70	Flint	18.00
Flint	87.00		
Tin Oxide	45.00		

The hand-built pottery is much appreciated by the art critics. This comprises the methods in use at Newcomb.

While it is necessary constantly to endeavor to perfect methods and to look for better ones, we feel that the decorator or maker of pottery should first turn his attention to the artistic problems, so that the nature and character of the production may direct the method. That the nature and character must include its usefulness and appropriateness as well as beauty, goes without saying.

Newcomb College
New Orleans, La.

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ORIGINAL PAPERS

THE PLASTIC PROPERTIES OF ENAMEL SLIP

BY R. D. COOKE

ABSTRACT

A simplification of the Bingham Plastometer, applicable to enamel slips, is described and the theory of plasticity discussed briefly.

It was found that increase in temperature or increase in water content of enamel slips raised the mobility without greatly affecting the yield value. Addition of clay and of certain inorganic salts raised the yield value without changing the mobility. Sodium silicate reduced the yield value to zero and lowered the mobility.

There have been numerous attempts to evaluate the consistency of enamel slips by various methods, most of which depended on some form of viscosity measurement. Bingham[1] has recently pointed out that all attempts to measure the viscosity of suspensions of solids in liquids have been based on the erroneous assumption that these suspensions behaved like true liquids. He has shown that under different conditions of pressure and size of capillary different apparent viscosities will be found because these plastic materials are in reality soft solids, and that solids require that the elastic limit or *yield value* must be exceeded before they will begin to flow.

With this concept in mind it will be apparent that, considering the flow of a plastic solid through a capillary, if a number of different stresses (pressures) are employed a number of different rates of flow will be found which when plotted against the corresponding stresses will lie on a straight line. This line when extrapolated to zero rate of flow will not intersect the pressure axis at zero as would be the case with a true liquid. The intersection will be at some definite pressure, which is proportional to the yield value. This represents the minimum pressure required to start the flow with that particular capillary. The slope of the line represents the *mobility*, analogous to fluidity of a liquid, and gives a second property of plastic substances.

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[1] "Fluidity and Plasticity," McGraw-Hill, 1922.

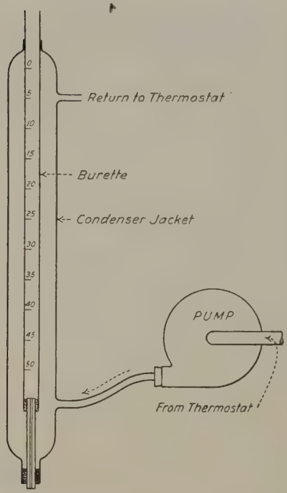

Fig. 1.

These two properties, yield value and mobility, completely define the characteristics and consistency of a suspension. They are independent of each other and cannot therefore be combined into a single expression as has been assumed in so-called viscosity measurements.

In practice, to make measurements on different instruments comparable, it is convenient to express the stress in dynes per square centimeter, taking into consideration the dimensions of the capillary. The theoretical details are discussed fully by Bingham.[1]

It became apparent that enamel slips fall into the class of plastic solids according to these conceptions. In practical terms the yield value is that property of enamel which causes it to hold its form up to a certain thickness when applied to ware in spite of definite forces (gravity, inertia and centrifugal force) tending to make it flow. It is the property commonly spoken of as shortness. The mobility has a less important practical bearing, but it is the property which makes an enamel flow more or less readily under forces greater than the yield value. The desirable condition of an enamel is a yield value commensurate with the thickness of coating desired, and a high mobility. A knowledge of the yield value and mobility of enamel slips explains their working properties in a perfectly logical way.

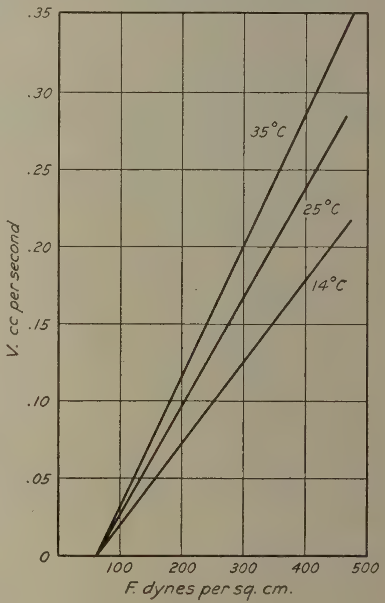

Fig. 2.—Effect of varying temperature.

A few determinations of these two properties have been made on typical enamels under different conditions, and while not complete nor of particular interest in themselves the method used may be of interest to those desiring to follow out these concepts of plasticity. The apparatus in the form used by Bingham was found unsuitable because the very small capillary tubes were arched over and stopped up by the larger particles of enamel frit. When larger tubes were used it was found that the pressures required were so low that they could not be controlled accurately.

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[1] "Fluidity and Plasticity," McGraw-Hill, 1922.

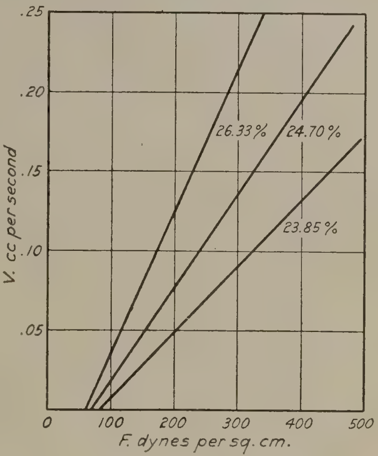

FIG. 3.—Effect of varying water content.

A modification was adopted which, while less exact, made use of the identical principles, gave good results and was several times more rapid. Referring to Fig. 1, the enamel slip was placed in a burette having the stop-cock replaced by a rather large capillary tube. The burette was enclosed in a water jacket through which water from a thermostat was pumped to maintain constant temperature. The enamel was previously brought to the same temperature by letting it stand in the thermostat in a flask. As the enamel flowed from the burette through the capillary the pressure due to the hydrostatic head was decreasing and the rate of flow was also decreasing. By taking the average pressure and the average rate for each five cubic centimeters outflow, data were available for plotting a curve from which the yield value and mobility could be read. The times at which the top surface of the enamel passed zero, five cubic centimeters and each multiple thereof were taken with a split hand interval timer. The corresponding average height or hydrostatic head for each interval was the distance from the lower end of the capillary to the 2.5, 7.5 cc. marks, etc.

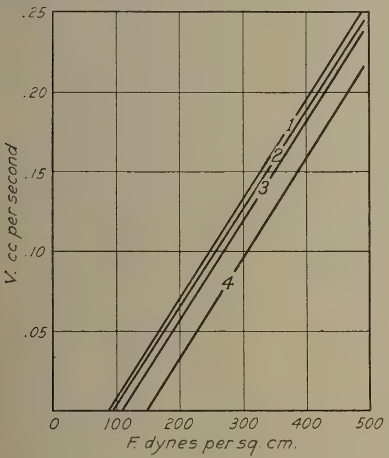

FIG. 4.—Effect of varying clay content.

1—4%	3—6%
2—5%	4—7%

Following are the data for the instrument and the record of a typical run.

F—the shearing stress in dynes per square centimeter $= \dfrac{RhDg}{2 \times l}$

where R = radius of capillary—.09247 cm.
h = height of enamel in tube in cm.
D = density of enamel.
g = 981, gravitational constant.
l = length of capillary—9.27 cm.

Cc.	*t*	*Dt*	*r*	*h*	*F*
0	0	.....	.....	....	...
5	23.4	23.4	0.214	54.6	491
10	47.9	24.5	0.204	49.9	449
15	75.6	27.7	0.181	45.3	407
20	107	31.4	0.159	40.6	365
25	143	36	0.139	36.0	324
30	186	43	0.116	31.4	282
35	238	52	0.096	26.8	241
40	308	70	0.071	22.1	199
45	415	107	0.047	17.4	156
50	615	200	0.025	12.7	114

Density of slip = 1.838.

All of these quantities were constant except the density and the series of h's, which were the same for every run. In a typical run the following values were tabulated. *Cc.* = burette reading; t = time in seconds; Dt = time interval in seconds; r = rate of flow in cc. per second = $5/Dt$; h = height of column in cm.; F = shearing stress in dynes per square cm. The values for r and F were plotted against each other on cross section paper, and the result was an approximately straight line intersecting the F axis at the yield value, f. The slope of the line, $\frac{r}{F-f}$ multiplied by a constant equal to $\frac{4}{\pi R^3}$ equals the mobility. The above example is shown plotted in the 14° curve on Fig. 2. The yield value was 64 dynes per square cm. and the mobility .8551. It is possible to determine the yield value algebraically from the data, but the graphic method is much to be preferred.

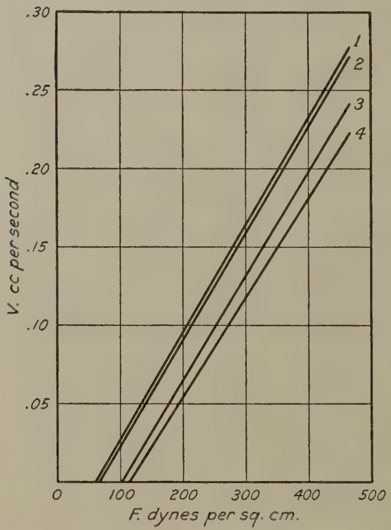

FIG. 5.—Effect of adding magnesium sulphate.

1—none 3—.050%
2—.025% 4—.075%

The accompanying charts show the effects of varying certain conditions on the characteristic curves for enamel slips.

Figure 2 shows that raising the temperature from 14°C to 35°C, increased the mobility 60% without changing the yield value.

Figure 3 shows that increasing the water content from 23.85% to 26.33% increased the mobility 120% and reduced the yield value 26%.

Figure 4 shows the effect of increasing the clay content. The yield value was increased without changing the mobility.

Figure 5 shows that addition of magnesium sulphate raised the yield value without changing the mobility materially.

The effects of a number of inorganic salts in chemically equivalent quantities were investigated. It was found that sodium chloride, sodium carbonate, sodium acetate, sodium thiosulphate, ammonium chloride and ammonium carbonate increased the yield value slightly without changing the mobility. Borax, acetic acid, aluminum chloride and cobalt nitrate increased the yield value considerably without changing the mobility. Magnesium sulphate, barium chloride and calcium chloride increased the yield value enormously and also reduced the mobility. Sodium silicate reduced the yield value to zero and decreased the mobility.

This method for determining the plastic properties of enamels suggests the interesting possibility of studying different clays in this light and determining what properties are desirable for a suitable enameling clay. Bingham[1] has shown that when a given suspension is studied in a wide range of concentrations two other properties appear—the concentration of zero yield value and the concentration of zero mobility. The former is thought to be related to the adsorptive power of the solid for the liquid or the proportion of adsorbed liquid to free liquid. The latter is probably related to the pore space and the distribution of particle size. A study of these properties would unquestionably add much to our understanding of the physical characteristics of ball clays.

Columbian Enameling and Stamping Co.,
Terre Haute, Ind.

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[1] *Jour. Ind. Eng. Chem.*, **14**, 1014 (1922).

THE OXIDATION OF CERAMIC WARES DURING FIRING.—V. A QUANTITATIVE STUDY OF THE NATURE OF SULPHUR EVOLUTION IN KILN FIRING.[1] (PART 2)

By Frederick G. Jackson[2]

Test on a Refractory Kiln

In the previous tests the analyses of CO_2, coal, and ash were from too small samples. The kiln temperature was measured at only one point. The ratio of SO_2 to SO_3 was not determined; and the test was stopped at 1680°F crown temperature.

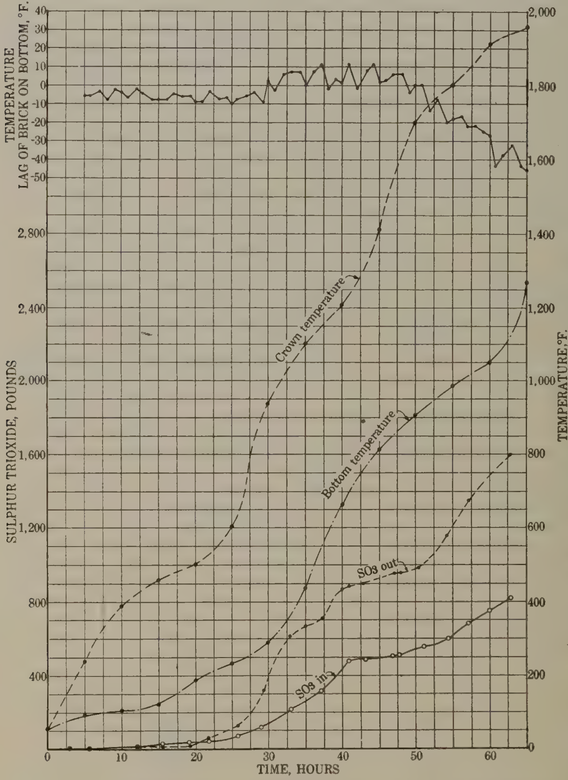

Fig. 7.—Cumulative weights of SO_3 and temperature in kiln.

The U. S. Bureau of Mines in coöperative work with the Refractories Manufacturers Association was studying the burning practice at a plant using a fire clay which contained sulphur and considerable iron. Part of the routine of the crew consisted of making (1) accurate temperature measurements of many parts of the kiln; (2) taking repeated samples of coal and ash and (3) drawing a continuous sample of flue gas which was averaged and analyzed each half hour throughout the firing.

The kiln was round down-draft, 26 feet in diameter with single outside stack. It was set with 40,950 nine-inch equivalents, having a fired weight of 273,500 pounds. The kiln was fired to 2150°F in 80 hours. Ten whole brick draw trials were set on the floor of the kiln, and ten more were arranged at a height of 4 feet from the floor. One from each set was drawn every 8 hours of the burn.

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[1] Published by permission of the Director, U. S. Bureau of Mines. For Part I of this paper see *Jour. Amer. Ceram. Soc.*, **7** [8], 634 (1924).

[2] Associate chemist, Ceramic Station, Columbus, Ohio.

Determination of Temperature Lag A green brick was drilled from the end to the center for insertion of a thermocouple. This brick was set on the kiln floor near the middle. Another thermocouple exposed to the kiln gases was put beside it. The difference in temperature readings of the two couples gave the temperature lag of the brick.

Only the significant data are presented. These are shown in Figs. 7 and 8.

Figure 7 shows (1) the cumulative weight of SO_3 entering the kiln; (2) the cumulative weight of SO_3 leaving the kiln; (3) the temperature of the bottom of the kiln; (4) the crown temperature; and (5) the lag curve of the brick on the bottom of the kiln. Figure 8 shows the cumulative weight of SO_2 entering and leaving the kiln.

Absorption of Sulphur by Ware The small amount of absorption of sulphur by the ware during "water-smoking" will be noticed at once. This is due principally to the bone-dry condition of the ware, to the grade of coal used, and to the rapidity with which "water-smoking" was accomplished. The coal contained only 0.90% of volatile sulphur. There was consequently very little sulphur entering the kiln during the 22 hours of light firing. The 250 to 450% excess air during this period indicated a good draft which swept out the sulphur gases.

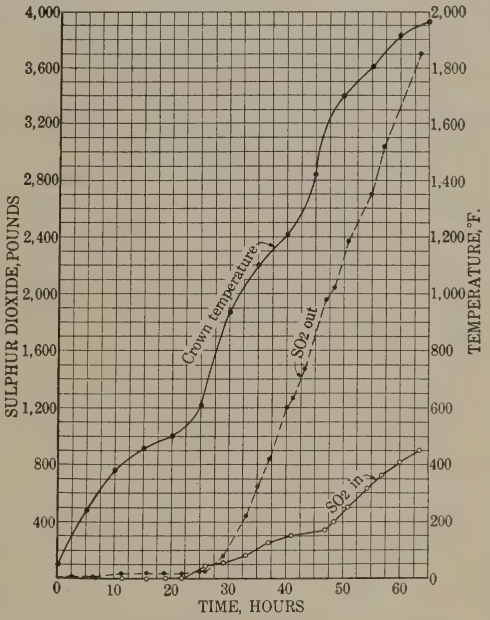

FIG. 8.—Cumulative weight of SO_2 in kiln.

Crown Samples of Gas Between the 28th and 42nd hours 790 pounds of sulphur seemed to have entered the kiln. Only 351 pounds of this were from the coal. At the 28th hour the excess air was 80%. This made a comparatively still atmosphere in the crown of the kiln, while at the same time the pyrite was decomposing vigorously. The SO_3 and SO_2 thus evolved evidently enriched the sulphur content of the crown gas samples.

Proportions of Gases Evolved An interesting study of the effect of the amount of excess air is seen in the evolution of gas between the 26th and 33rd hours—498 pounds of SO_3, and only 393 pounds of SO_2 were evolved. There had been a large excess of air up to the 26th hour, and its effect must have persisted for a little while, so that in the first part of the firing of the pyrite SO_3 formed more than half of the product. Beyond this period oxygen was rare in the kiln. The tendency was therefore to form the compound requiring less oxygen. Between the 33rd and 51st hours 350 pounds of SO_3 and 926 pounds of SO_2 were formed. The ratio of SO_3 to SO_2 is changed from 1:0.79 to 1:2.64. Between the 51st and 63rd hours more SO_3 comes off—630 pounds of SO_3 and 1317 pounds of SO_2. The ratio here is 1:2.09. This increase in the ratio of SO_3 evolved may be due to the catalytic effect of the hotter ware in the lower part of the kiln. It may also be due to the source of the gas, the decomposition of sulphate rather than pyrite. The high ratio of SO_3 during the first of these stages is not explainable on the basis of results found in the second paper of this series; it can best be explained by a selective absorption of SO_2 in preference to SO_3 by the Fe_2O_3 contained in the cooler parts of the ware. When any such absorption takes place, an oxidized iron sulphur compound is formed. It has already been shown that under similar conditions, oxidized compounds decompose at higher temperatures than pyrite, and with the evolution of a higher ratio of SO_3 to SO_2.[1]

Lag Curve The temperature difference between the inside and the outside of a brick at the bottom of the kiln is interesting.

At 30 hours the inside of the brick is for the first time hotter than the kiln atmosphere. At this stage, SO_3 is passing out of the kiln in considerable volume. As this gas penetrates the ware, some of it is absorbed as sulphuric acid and ferric sulphate. The heat generated by these reactions is considerable, and would account for the negative lag. Sulphur dioxide, similarly oxidizing and reacting will have the same effect, and may account in part for the negative lag up to the 42nd hour.

A temperature of 770°F at the 43rd hour probably started the pyrite in the brick to burning. The heat of combustion of the sulphur continued to hold up the temperature inside the brick above that outside until the 51st hour. The decomposition of ferric sulphate is slow, and does not generate appreciable heat, consequently the inside temperature lagged at the last.

Sulphur Balance Since this test was not carried out to the end of sulphur evolution, an actual balance of sulphur cannot be made. The amount of sulphur in all forms at each hour of the test can, however, be found. This is interesting for comparison with a similar curve in the previous test.

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[1] In the second paper of this series it is shown that ferric sulphate in 100% excess air evolved only 15% of its sulphur when heated to 1040°F and then decomposed rapidly. At 1427°F it had evolved 44% of its sulphur as SO_3 and 29% as SO_2. Coarse pyrite under the same conditions evolved 1.30% of its sulphur as SO_3 and 63% as SO_2 between 797 and 833°F.

Sulphur entering the kiln was calculated from the amount of coal fired and the percentage of sulphur therein. Sulphur leaving the kiln was calculated from the weights of SO_3 and SO_2 found by analysis of blue gases. Total sulphur in the ware was estimated at 1.1% from results shown in the next section. There were 3009 pounds of sulphur in the green ware.

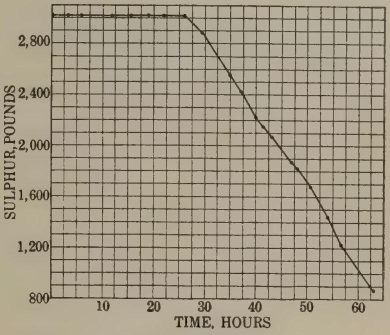

Fig. 9.—Sulphur content of kiln.

The results as shown in Fig. 9 are very different from those on the previous kiln. (Compare Fig. 6.) In that test the ware contained little sulphur, the coal was high in it, and the heating schedule was slow. All three of these factors were reversed in the present test. Added to these is the difference in the character of the two clays. Consequently, the amount of sulphur absorbed was much less. Whereas in the first test 338 pounds, or 27.4%, of the sulphur already in the ware was absorbed, in this test the greatest amount absorbed was 10.8 pounds in 19 hours, or 0.35%. The evolution of sulphur was maintained at an almost constant rate from the time it began, at the 26th hour, until the end of the test. This rate would indicate that all sulphur was out of the kiln by the 76th hour. The kiln was fired for 80 hours.

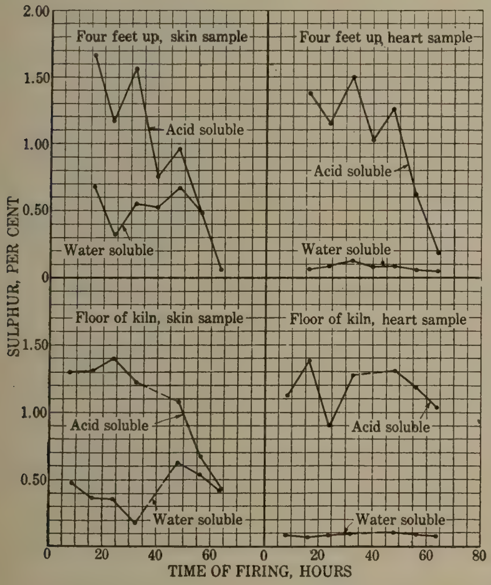

Fig. 10.—Per cent of sulphur in ware.

Draw Trials

Two brick draw trials were taken from the kiln every 8 hours. One row had been set 4 feet above the floor in the kiln, the other row on the floor. These bricks were analyzed as in the previous work, a skin sample and a heart sample from each. Water-soluble and dilute aqua regia-soluble sulphur were determined.

TABLE II—DRAW TRIALS FROM 4 FEET UP IN KILN

	Skin samples			Heart samples		
Time fired, hours	Water-soluble sulphur	Acid-soluble sulphur	Per cent total sulphur	Water-soluble sulphur	Acid-soluble sulphur	Per cent total sulphur
8		No sample			No sample	
16	0.681	0.978	1.659	0.078	1.306	1.384
24	0.308	0.876	1.184	0.098	1.047	1.145
32	0.539	1.020	1.559	0.125	1.479	1.599
40	0.524	0.223	0.747	0.086	0.949	1.035
48	0.674	0.301	0.975	0.080	1.207	1.287
56	0.393	0.006	0.399	0.058	0.580	0.638
64	0.057	0.001	0.058	0.042	0.153	0.195
		DRAW TRIALS FROM FLOOR OF KILN				
8	0.487	0.813	1.300	0.092	1.035	1.127
16	0.352	0.964	1.316	0.067	1.324	1.391
24	0.357	1.043	1.400	0.083	0.818	0.901
32	0.192	1.031	1.223	0.092	1.197	1.289
40		No sample			No sample	
48	0.622	0.464	1.086	0.103	1.204	1.307
56	0.541	0.135	0.676	0.099	1.097	1.196
64	0.409	0.009	0.418	0.089	0.964	1.053

The percentage of sulphur found on a basis of ignited ware is given in Table II and these results are also shown by curves in Fig. 10.

Discussion of Draw-Trial Analyses

Water-Soluble Sulphur

The analyses of skin samples of draw trials from 4 feet up in the kiln illustrates clearly the two processes of gas absorption. At 16 hours the amount of water-soluble sulphur is great owing to the sulphurous acid held in solution by the hygroscopic water. At 24 hours, even though this water was not expelled, the solubility of SO_2 in it had been diminished by the increase in temperature. This increase in temperature, however, increased the tendency to form ferric sulphate, so that the amount of water-soluble sulphur increased again until the temperature was so high that it drove off first the free sulphuric acid and then that combined as ferric sulphate. This decomposition was nearly completed in 64 hours. The surface of the ware at the bottom of the kiln shows the same course of events, but taking place more slowly and not going to completion.

Samples from the hearts of the brick show a gradual increase to a smaller maximum, and then decrease again. Once the sulphur gases had penetrated the ware they were more easily retained there, and were converted from the acid condition to ferric sulphate.

Acid-Soluble Sulphur

It would appear from these results that the pyritic content of the clay was very irregular. No theory of kiln absorption of sulphur has been advanced by which there might be formed during firing a compound insoluble in water but soluble in dilute aqua regia. Such a reaction is unreasonable. However, the results diverge unreasonably. The 14 analyses made from samples fired for 32 hours or less show a minimum of 0.813% of sulphur, and a maximum of 1.559%; the average is 1.080%. It is, therefore, probable that the distribution of pyrite is very irregular.

Half-way down the kiln the pyrite was all burned out of the surface of the ware well before the test was completed, and almost entirely out of the middle of the ware by the end of the test. The decomposition of pyrite on the surface of the ware on the floor of the kiln was finished, but decomposition of pyrite at the center of the kiln hardly begun.

Summary

The results of these four kiln studies may be summarized as follows:

1. A considerable proportion of the volatile sulphur from the coal used is absorbed by the ware as it passes through the kiln until a temperature of about 1400°F is reached. This absorption takes place in different ways, as the temperature rises as follows:

(*a*) Sulphur dioxide is absorbed by surface moisture on the ware as H_2SO_3, up to 212°F; after which H_2SO_3 is decomposed.

(*b*) Sulphur trioxide is absorbed by surface moisture on the ware as H_2SO_4. The H_2SO_4 attacks the accessory minerals, especially the lime and iron. This absorption ceases at 212°F, but the H_2SO_4 is not decomposed by heat until about 500°F is reached.

(*c*) Ferric sulphate is formed throughout the ware at temperatures up to 1100°F by the action on free ferric oxide in the ware of either absorbed acid solution or kiln gases.

(*d*) Sulphur is locked in the clay in an insoluble form, possibly as a sulpho-silicate, at all temperatures up to 1300°F under conditions favorable to such action.

2. Sulphur is evolved from the kiln and passes off up the stack from the following causes:

(*a*) Sulphur gases from the coal not absorbed by the ware. (The ratio of SO_2 to SO_3 may be changed by the catalytic action of the hot clay as the gas passes through the kiln.)

(*b*) Sulphur dioxide from H_2SO_3 at 212°F and breaking down of any sulphites temporarily formed.

(*c*) Vaporization and breaking down of H_2SO_4 at about 500°F.

(*d*) Decomposition of pyrite and associated minerals. This is often the main source of sulphur in stack gases after (*a*) above. This begins at about 800°F, and takes place vigorously.

(*e*) Decomposition of ferric sulphate. This gives off the bulk of its gas between 1040° and 1427°F.

(*f*) Decomposition of ferrous sulpho-silicate probably beginning at about 1300°F.

3. Evolution of sulphur may be temporarily suspended by the ignition of carbon in the kiln, which is often brought about by the burning pyrite. The carbon in burning will retard the oxidation of pyrite until the former is nearly all burned out.

4. A core may be formed in partly fired ware when pyrite is burned out on the surface, but remains at the center. This core disappears on further firing.

5. A different core may be formed by too rapid firing. If there is much permanently combined sulphur (sulpho-silicate) present, and the ware loses much of its porosity on the surface before the sulphur is all decomposed, SO_2 and SO_3 will be unable to escape as fast as generated, and will set up a pressure. This will swell the ware. Ferrous silicate will then melt to a black mass, full of blebs, at the center, although the surface of the ware may be the color of properly fired ware.

Acknowledgments: Thanks are due to the managements of the various plants visited for the courtesies extended by them; also to E. E. Pressler of the Columbus Experiment Station for help in taking samples in the second investigation; to Robert Armstrong in the third investigation; and to the crew of the car "Holmes" in the fourth investigation.

THE LABORATORY TESTING OF ALUMINOUS REFRACTORIES[1]

By R. F. Geller

ABSTRACT

Eight brands of high alumina refractories and two brands of fire clay refractories, which are used by the trade under conditions of service requiring resistance to the corrosive action of lime and cement clinker at high temperatures, were subjected to standard and modified laboratory tests for high grade refractories. Data obtained indicate the results which may be expected in the technical examination of this type of product.

The great demand for refractories capable of meeting the increasing severity of furnace conditions, and the high cost of the so-called special refractories, have compelled manufacturers to focus their attention on the production of modified fire clay refractories to obtain from them the very highest efficiency consistent with their inherent physical and chemical properties. For certain types of service this has resulted in the rapidly increasing use of high alumina or bauxitic materials.

Since the literature contains very little data on the laboratory testing of refractories containing fifty per cent or more of alumina, a preliminary investigation was carried out at the Bureau of Standards on a limited number of brands to find out the behavior of such materials when subjected to standard and modified tests.

Complying with a request from the Bureau, five manufacturers submitted shapes used in the lining of rotary cement kilns. These samples, representing two brands of fire clay refractories and eight brands of aluminous refractories, were subjected to the following tests: A. Softening point; B Constant volume; C. Quenching; D. Absorption; E. Deformation under load; F. Slagging.

Method of Testing

Softening Point The softening points were determined in an electrically heated muffle and measured by means of Orton pyrometric cones.

Constant Volume The constant volume test was made by heating test pieces at 1400°C for five hours and measuring the resultant change in linear dimensions. Five test pieces[2] of each brand were used in this test.

Quenching The quenching test was conducted on brick which had been reheated at 1400°C for five hours. The quenching itself followed in principle the tentative A. S. T. M. method. It was carried out by heating the brick at one end to 850°C in a kiln door

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[1] Published by permission of the Director of the Bureau of Standards of the U. S. Department of Commerce. Received Jan. 28, 1924.

[2] The test pieces were sawed from the shapes submitted and approximated the size and shape of nine-inch brick.

and plunging the hot end into a bath of running water to a depth of four and one-half inches. The brick were allowed to remain in the water for three minutes, taken out, allowed to steam in the air for five minutes, and then returned to the kiln door. This was repeated in hourly cycles until the end had entirely spalled off. Five test pieces[1] of each brand were quenched.

Absorption The absorption was determined on the material as received and also on the test pieces which had been reheated at 1400 °C for five hours. The following formula was used:

$$\text{Per cent absorption} = \frac{\text{Saturated weight} - \text{Dry weight}}{\text{Dry weight}} . 100$$

Deformation Under Load Several load tests were made in accordance with the A. S. T. M. standard method, but the results showed uniformly high resistance to deformation. The test was, therefore, made considerably more severe by holding the test pieces at 1450 °C for one and one-half hours under a load of forty pounds per square inch. This modified test, as the data in Table II show, was conducted on test pieces[1] as received and on test pieces[1] which had been reheated at the Bureau at 1400 °C for five hours.

Slagging The slag test was made in two ways:

1. A heavy cardboard cylinder one inch high and two inches in diameter was placed on the upper face of a test piece[1] laid flat and the cylinder was filled level full with cement clinker ground to pass a 100-mesh screen. The test set was then placed in the furnace, heated to 1400 °C and held at this temperature for five hours. The resistance to slagging was determined by visual inspection.

2. Cones were prepared of mixtures of equal parts of the refractory to be tested and of the clinker. Both were ground to pass an 80-mesh screen. The softening points of the mixtures were then determined according to the A. S. T. M. standard method.

Results

The data obtained from these tests indicated that the refractories submitted belonged to three well defined groups. Figure 1 and Table I have been so arranged as to emphasize this grouping.

Softening Point The data show a close relation between alumina content and softening point and, as is to be expected from the nature of the SiO_2-Al_2O_3 softening point diagram, the refractoriness increases rapidly with increase of Al_2O_3 in this range of compositions.

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[1] The test pieces were sawed from the shapes submitted and approximated the size and shape of nine-inch brick.

TABLE I

Type of test	Specimens containing 40–45% Al_2O_3		Specimens containing 50–55% Al_2O_3		Specimens containing 70–85% Al_2O_3	
	Body no.	Results	Body no.	Results	Body no.	Results
Softening point	8	29	2	34	1	39
	9	30	4	34	3	37
Results given in cones			6	34	5	36
			11	34	12	37
Average		29+		34		37
Quenching test	8	6	2	8	1	50+
Results given as number of quenchings required to produce failure	9	3	4	22	3	19
			6	50+	5	19
			11	50+	12	40
Average		4.5		32+		32+
Per cent absorption after reheating at 1400°C for 5 hours	8	6%	2	14%	1	19%
	9	6%	4	14%	3	15%
			6	13%	5	14%
			11	15%	12	20%
Average		6%		14%		17%
Resistance to slagging	8	4	2	6	1	10
Results given in cones as softening points of 50–50 clay-clinker mixture	9	4	4	6	3	14
			6	6	5	14
			11	6	12	14
Average		4		6		13
Load test	8	Failed	2	3.7%	1	2.7%
Results given as per cent deformation under a load of 40 lbs. per sq. in. after heating at 1450°C for 1½ hours	9	Failed	4	4.5%	3	Failed
			6	7.0%	5	Failed
			11	4.8%	12	5.7%
Average				4.5%		4.2%
Constant volume	8	+0.1%	2	+0.2%	1	+0.3%
Results given as per cent linear change after reheating at 1400°C	9	+0.1%	4	+0.5%	3	−0.3%
		Note: both over-fired	6	−0.1%	5	−0.1%
			11	−0.2%	12	+0.1%
Average		+0.1%		+0.1%		0.00

With the exception of bodies 8 and 9, which are not, strictly speaking, in the class of aluminous refractories, the softening points are well above those of fire clay refractories intended for high heat duty and a softening point of cone 34 would apparently be a reasonable specification for the product considered in this investigation.

Constant Volume The uniformity of results obtained by means of the constant volume test for the ten brands examined, given in Table II, indicate that this test has very little if any value as a method for the determination of the relative qualities of high alumina refractories.

Quenching In the quenching test, bodies 8 and 9 which are relatively low in alumina (see Fig. 1 and Table I) showed poor resistance to spalling as compared with those containing from 50 to 85%. In the latter group the results do not show the close relation between softening point, chemical composition and resistance to thermal shock which was previously obtained with fire clay refractories.[1] This may be explained by considering the volume changes of free silica during heating and cooling[2] which, as is generally accepted, materially affect the ability of a refractory to withstand changes in temperature through the ranges in which these changes take place. If, therefore, all or practically all of the silica is combined with alumina in the finished product, these volume changes will no longer be the predominating factors affecting resistance to spalling and the influence of such factors as porosity, mechanical strength and structure become more pronounced. These in turn can be controlled by workmanship and method of manufacture.

TABLE II

Body no.	Per cent linear change in constant volume test	Per cent absorption as received	Per cent absorption after reheating	Per cent deformation under load as received	Per cent deformation under load after reheating	Per cent Al_2O_3 (data furnished by manuf.)
1	+0.3	18	19	2.64	2.0	70–75
2	+0.2	15	14	3.71	12.2	50–55
3	−0.3	15	15	Failed[1]	Failed[1]	80–85
4	+0.5	14	14	4.5	3.7	55
5	−0.1	14	14	Failed[1]	Failed[1]	75
6	−0.1	13	13	7.0	5.7	50
8	+0.1	9	6	Failed	Failed	40
9	+0.1	7	6	Failed	Failed	40
11	−0.2	13	15	4.81	4.01	50
12	+0.1	20	20	5.76	5.16	75

[1] Not characteristic load test failures.

The data on quenching (Table II) also show that wide variation in results was obtained with the bodies containing from 50 to 85 % alumina. Sample 2 failed after eight quenchings, while samples 1, 6 and 11 showed no indications of failure after fifty quenchings. There are no reasons evident for this, but it is quite probable that information of interest and value could be obtained through a detailed study of the raw materials and methods of manufacture involved.

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[1] R. F. Geller, "Progress Report on Specifications for Refractories," *Jour. Amer. Ceram. Soc.*, **6** [10], 1098–1111 (1923).

[2] α-quartz to β-quartz at 575°C; α-cristobalite to β-cristobalite at 230°C.

Absorption The complete absorption data are given in Table II. It is evident that reheating had very little effect on the absorption and in several cases no change could be determined by the method employed. For this reason only one set of results were plotted in Fig. 1. The lower refractory bodies (8 and 9) were comparatively dense and the structure after reheating showed evidence of the formation of glass, while the bodies of higher refractoriness were on the average, higher in absorption, but there is not sufficient difference between these and the bodies of average alumina content to be of significance. It is doubtful if any specifications based on absorption would be of value.

Load Probably the most important result of the load test work is the fact that the A. S. T. M. standard method requiring satisfactory resistance to a load of 25 pounds per square inch at a temperature of 1350°C for one and one-half hours was shown to be not sufficiently severe to produce good comparative data. For example, there was practically no difference in the amount of deformation of bodies 1 and 8, although most of the other tests of the series indicated a considerable difference between these two materials. This is not at all surprising since it is well known to manufacturers of refractories that a brick of many inferior qualities can be so made as to withstand satisfactorily the test for deformation under load at high temperatures. Accordingly, the temperature requirement was raised to 1450°C and the load to 40 pounds per square inch.

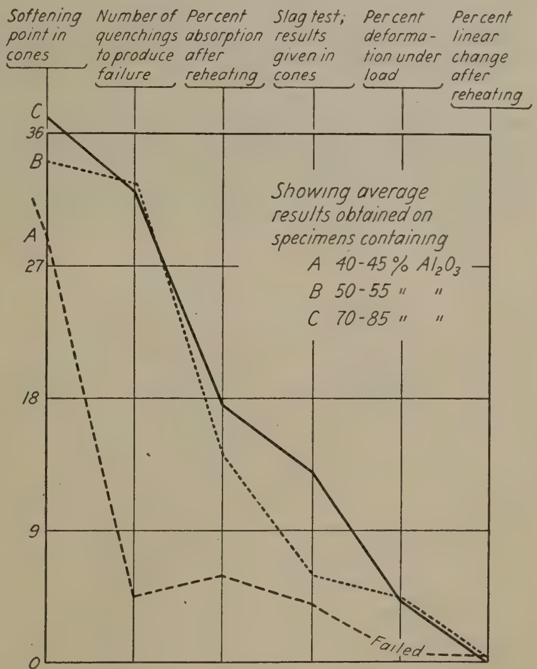

FIG. 1.

Table II shows that (with the exception of body 2 which also showed especially poor resistance in the quenching test) reheating had no noteworthy effect on the deformation of the test pieces[1] and only test results on material as received were plotted in Fig. 1. Brands 3 and 5 sheared under a load of forty pounds per square inch before the maximum temperature (1450°C) had been reached, but the appearance of the tested specimens would indicate that failure was due more to excessive load than to any appreciable lowering of viscosity in the material. Since resistance to a load of forty pounds per square inch is considerably greater than that of ordinary structural requirements, it is quite possible that these brands would not fail in service although their structure would undoubtedly be weakened at high temperatures. For this reason a further modification of the test, reducing the load to twenty-five pounds per square inch while retaining the temperature and time requirements of 1450°C and one and one-half hours, respectively, is recommended.

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[1] *Loc. cit.*

Lack of material prevented repeating the work, but it would seem reasonable to assume that such a test would eliminate the product which is sold to resist load and slag action at high temperatures, but which would not give satisfactory service. The data further indicate that a maximum allowable deformation of 5% would be a liberal specification, although more information would be required to determine definitely this value.

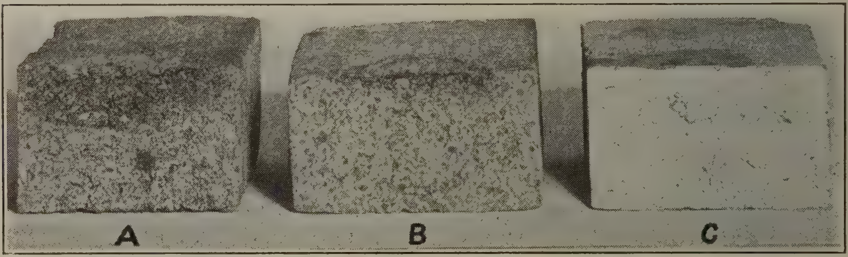

Fig. 2.

Slagging Typical results of the slagging test, conducted according to the first method described, are shown in Fig. 2. Specimen A (Body 9) contained from 40 to 45% alumina, specimen B (Body 11) from 50 to 55% alumina, and specimen C (Body 1) from 70 to 85% alumina. Although the results permit of easy comparison between the three groups, there being, for example, considerable fluxing action and penetration of slag in the case of A while C remained unaffected, the fact remains that the evidence obtained cannot be so interpreted as to show numerically the relative resistance to slagging.

For this reason the work was duplicated, using the second method. The results obtained (Table I and Fig. 1) seem to warrant consideration because: A, the values can be duplicated and are consistent with variations in alumina content; B, the test can be standardized; C, it affords a numerical ratio upon which a specification can be based.

Summary

The data obtained, as summarized graphically in Fig. 1, would indicate that with refractories of the aluminous type containing 50% or more alumina, the following results may be expected from laboratory tests:

1. The softening point will be equal to, or exceed, that of the Orton standard pyrometric cone 34.
2. The constant volume test will not produce results of value.
3. The refractory will withstand eighteen or more quenchings without failure.
4. The absorption, while generally higher than for refractories containing less than 50% alumina, would not be satisfactory for specification work.
5. The deformation will not exceed 5% when using a load of twenty-five pounds per square inch and a maximum temperature of 1450°C.
6. The softening point of a mixture of equal parts of refractory and cement clinker is equal to, or exceeds, that of the Orton standard pyrometric cone 6. This test would, of course, apply only to material intended for service requiring resistance to the slagging action of cement clinker.

SOME CONSIDERATIONS NECESSARY IN SELECTION OF REFRACTORIES FOR THE OPEN HEARTH[1]

By Sidney Cornell

ABSTRACT

The kind, quality and quantity of refractory brick used in steel plant furnaces, coke ovens, blast furnace, open hearth and auxiliaries are discussed.

The factors that influence the life of refractory brick in the open hearth furnace, discussed numerically, with the economic situation indicated in monetary value.

The Situation in General

Improper selection of kind and quality, and to a certain extent quantity of refractories has been the theme of more than one paper presented before the American Ceramic Society. Complaint has been made that failures are largely the consumer's own fault, and due to the fact that the refractories manufacturer is not given accurate and detailed analysis of actual conditions to which his product will be exposed.

The steel manufacturer will not or cannot place the desired information in the hands of the refractories manufacturer. There are several reasons, some of the most important of which will here be indicated. It behooves the refractories manufacturer to get the facts. Fortunately this is not as difficult an undertaking as might be supposed. Coördination of all facts is a difficult task. The large and important technical facts on refractories contributed by the Bureaus of Standards and Mines, the Mellon Institute, etc., in the past five or six years are but part of the consideration necessary. There are parallel situations existing in a number of different industries. Consideration of these situations should be of material aid.

A number of important improvements in metallurgical practices await improvement in refractory materials. The metallurgist cannot or will not clearly indicate to the ceramist just what to do or how to improve his products. This probably is due to the fact that metallurgists do not understand clays, etc. There are a number of refractories on the market which in their performance are excellent. On small apparatus, and on chemical engineering apparatus they are used with marked satisfaction, but for large furnace work their cost is prohibitive. If only a few thousand brick are required for a kiln, and oven, a fire box, or for small electric furnace linings, this high cost is of no great consideration.

An open hearth has 1,000,000 brick in it. Chrome and magnesite brick have been used for the past twenty years. It is all well and good to say and to know that chrome brick will stand up well under conditions where silica or magnesite will spall away 25%. Chrome brick cost today $210.00 per M ($45 net ton), whereas ten years ago they cost $110 per M. Our standard open hearth, if made of all chrome brick, would come to $200,000 for brick alone. First, second and third quality fire-clay brick, silica brick magnesite and chrome brick all have their specific places in an open hearth. They are used because no better material has been proven.

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[1] Presented at the Atlantic City Meeting, Feb., 1924 (Refractories Division).

Consider the industries where forging furnaces, annealing furnaces, carbonizing, hardening and draw-back furnaces, either muffle, direct, continuous, automatic or semi-automatic are used. The refractories in such are not exposed to the same exacting conditions found in melting furnace, blast furnace, open hearth, electric furnace or Bessemer. While some betterment is still possible in these heat treating furnaces, as a rule their life is long. Once built they stay built. From a refractories standpoint the open hearth is rebuilt at least once yearly, and the blast furnace which should have produced 1,000,000 tons per lining, is rebuilt once in five or six years. Coke ovens have lasted as long as 20 years, although this is exceptional.

It is generally believed that refractories fail because they shrink and spall, not because they melt. This is begging the subject. We can expect refractories to meet present conditions only by knowing the conditions to be met, by a complete and thorough study of all conditions, consideration being given to economic conditions, costs, etc.

No open hearth furnace is going to be built from chrome brick alone at a cost of $200,000 for brick. Some of the excellent refractories obtainable cost many times more than chrome brick. Common brick at $22, 1st quality clay refractories at $42, silica at $40, chrome at $210, and magnesite nearly $300 per thousand are used as experience has proven the economies in the use of each.

The open hearth furnaces use several fuels, natural gas, producer gas, coke oven gas, oil or tar and powdered coal. Powdered coal would be an economy if refractories were obtainable that would withstand its use. Coke oven gas cannot be burned as cheaply as producer gas because of the limitations of refractories. Powdered coal is an economic failure in open hearth work today simply because of the failure of the refractories.

The Life of Refractories

An open hearth is operated so that two heats per day are gotten out of it. Naturally if three heats are possible they are run. Sunday practice makes use of a soaker heat, charging cold pig. An open hearth roof is estimated to last 250 heats, and checkers on producer gas 500 heats. Thus a furnace turning out 11 or 12 heats per week has a roof life of 20 weeks. A new roof is then built. It commonly requires one week to replace the first roof, and two weeks to make the rebuilding, a loss of three weeks in time, and a production of 3600 tons of steel. While 250 heats per roof are looked for, this is not always attained.

The consumption of refractories in an open hearth depends largely upon the fuel used. The following are estimated lives:

Life of checkers on natural gas 1000 heats, producer gas 500, oil 500 and powdered coal 250.

Industrial Requirements

A comparison with other steel plant apparatus is desirable for a complete understanding of the overall situation as affecting open hearth refractories.

Coke Ovens Generally satisfactory. Extremes are found in old original Koppers by-product coke oven construction, dating back to 1909–10, and the Semet-Solvay, whose ovens have lasted as long as 20 years in operation.

Koppers by-product ovens require 20 tons structural steel per oven, 150 cu. yds. concrete, 35,000 brick, 190 shapes and sizes of silica brick and 50 shapes and sizes of fire-clay brick.

Semet-Solvay by-product ovens require 26 shapes and sizes of silica brick and 9 shapes and sizes of fire-clay brick.

Blast Furnaces Generally satisfactory. Records of high production on a lining easily obtainable. Records of failure more difficult to locate. The failures probably yield more data than average performance records. Standard 500–600-ton furnace, 14′ hearth, 10′ well, 21′ × 13′ bosh, stock line 15′, stack proper 45′. Hearth 1700 cu. ft., bosh 3300 cu. ft., stack 12,000 cu. ft.

BLAST FURNACE BRICK

	Number of shapes and sizes	Number of pieces
Hearth and bosh	9	55,000
Inwall	4	135,000
Top and gas arch	10	50,000

Total, 23 shapes and sizes, 3 qualities and 240,000 pieces. In 9-inch equivalents, this will total 500,000 brick.

Blast Furnace Stove, McClure Type One stove contains 38 shapes and sizes, 50,499 pieces, 1st quality clay, and 40 shapes and sizes, 89,690 pieces, 2nd quality clay brick.

The four stoves to a furnace thus contain 78 shapes and sizes, 2 qualities and 560,000 brick.

A blast furnace as iron producing apparatus contains 100 shapes and sizes, 5 qualities of brick, 800,000 individual pieces, and which in 9-inch equivalents totals 1,500,000 brick.

It is the practice when specifying a lining to add 5% to net count for losses in building. This in itself is a high requirement and should be unnecessary. It is the practice of (H. & W.), one well-known refractories manufacturer, to stamp brick for hearth H, for inwall I, and for top T. This practice should be adopted for open hearth brick,

A single open hearth furnace has as many brick in its structure as a blast furnace, a fact not often appreciated.

As an example of failure: Duquesne No. 5 was blown in on March 16, 1909, and out August 24, 1910, having made approximately 200,000 tons of iron. The last word in engineering was put into that furnace, but it did not come out. Why did the furnace fail? What did the brickmakers learn from this failure? There are many records of 1,000,000 tons production on a lining.

The Open Hearth A furnace can be assumed to contain some 300 tons of structural steel in its pan, binding, crane runways, etc.

Natural gas, basic bottom 80-ton-furnace contains:

	Number of shapes and sizes	Number of pieces
Silica brick	26	141,000
Magnesite brick	3	20,000
First quality clay brick	16	250,000
Third quality clay brick	7	84,000
Common brick	1	350,000
Grain magnesite	80 tons	

In such a furnace there are five grades of brick, 53 shapes and sizes and 845,000 individual pieces. In 9-inch equivalents this will total over 1,500,000, equal to the brickwork of a blast furnace and stoves.

Five grades of brick are required in its structure. Considering the work it has to perform these seem too few.

Producer gas, acid bottom 80-ton furnace contains:

	Number of shapes and sizes	Number of pieces
Silica brick	20	197,000
1st quality clay brick	16	250,000
3rd quality clay brick	7	84,000
Producer (2) and gas mains	7	40,000
Common brick		350,000
Bottom sand	25 tons	

In such a furnace there are 5 grades of brick, 50 shapes and sizes and 921,000 individual pieces.

The auxiliaries in connection with the open-hearth furnace are relatively simple in refractory requirements.

A metal mixer will use 2nd quality fire-clay brick for its lining, using 24 shapes and sizes and 50,000 pieces.

Calcining cupolas will utilize 1st quality fire-clay brick, some common brick using 3 shapes and sizes and 10,000 pieces.

Ladles utilize ladle brick, a 60-ton taking 2700 pieces, and an 80-ton, 3500.

Refractories Requirements of Open Hearth vs. Blast Furnace

In round numbers the blast furnace consumes one brick per ton of iron made. In round numbers the open hearth consumes three brick per ton of steel made when on natural gas; 5 to 6 brick per ton of steel made when on producer gas; 8 to 12 brick per ton of steel when on powdered coal.

A production of 1,000,000 tons of open hearth steel using natural gas as fuel and the easiest on brick represents:

Expenditures

Material other than brick	$ 25,000
Brick	160,000
Labor	115.000
	$300,000

It may be roughly stated that it cost $.30 per ton of steel for refractories using natural gas as fuel, $.60 using producer gas, and $1.20 per ton using powdered coal.

A blast furnace producing 1,000,000 tons of iron may require $.15 per ton of iron for rebuilding. If, however, a blast furnace fails as did Duquesne No. 5, the refractory cost will jump five times, namely to $.75.

With an open hearth roof which is expected to last 250 heats, if the performance is 80 heats to a roof, and 125 heats the final performance, the normal cost climbs from $.30 to dollars per ton of steel made. It is not to be wondered that the steel metallurgists are complaining.

Chrome brick was mentioned but was not listed in open hearth construction. Chromite brick during the war and immediately thereafter became so unsatisfactory that open hearth builders found that it was not necessary to separate magnesite from silica. A great loss of chrome brick business resulted. Poor quality of home ores may have been the reason. The merits of good chrome brick, non-sticking, non-melting, hot-patch merits, resistance to spalling, are known and advertised. Ten times the life of silica is a broad statement. On a cost to cost basis it must be $40 to $210 to start with, or 1 to 5.

Performance of Refractories

Complaint has been made that the steel manufacturers do not keep records of performance of refractories. Ten years ago practically every master mason in a steel plant kept or attempted to keep card records covering receipt of brick, shed location, in and out record, placement in furnace, etc. This is no mean job of accounting or of clerical work. The steel business is peculiar when it comes to recording. The modern automobile shop, taken as representative of specialized manufacture, has a planning, a cost and an inspection department, which function in a way impossible, so it seems, in a steel plant. High grade clerks, properly paid, are employed in the automobile shop. As a rule the clerk given to a master mason, in a steel plant, especially if his own selection, is a bright young bricklayer, more interested in laying brick than in keeping records. If an honest-to-goodness clerk is employed, his pay is small, comparatively speaking. Here and there, there are reliable refractories records. Usually when they exist, because of their merit, and the steel works management refrains from disclosing them to Tom, Dick and Harry.

The refractories manufacturer must make it easier to record refractories. Stamping of "hearth," "bosh," "inwall" and "top" on the brick would help materially. Open hearth brick might be stamped "roof," "checker," "neck" and with a code letter, heat number, etc. A sufficient number of brick will probably be salvaged with identification marks so that records of their life could be had.

Whereas the automobile industry is well equipped with cost, production and inspection clerks, and likewise with competent metallurgists, the steel business is deficient in them. Perhaps unnecessary importance is attached to steel works cost records such as they are. This may explain why the steel plant management has so reluctantly given out refractory performance. As an example of this situation, and one that contributes some information on refractories, the following is representative:

A well known steel plant has 24 50-ton open hearth furnaces, using natural gas as fuel. 16,788 heats were made in 12 months.

Classed as refractories are magnesite, dolomite, chrome ore, loam, clay and coke, a total of 50,000 tons of these materials being used annually. Indirectly the performance of the refractory brick influences this consumption. In the year, 1,000,000 ladle brick, 19,000 stopper, 200,000 sleeve and 19,250 nozzle brick were used, which are not influenced by the performance of the furnace brickwork.

During the year 80 repairs were made to the furnaces. A repair is either a new roof, or a complete rebuilding.

In the record, one of the furnaces lasted only 79 heats and the roof was gone, whereas another furnace lasted 318 heats on a roof. The average for the 24 furnaces was 189 heats per roof. The question all would like to be able to answer is why did one furnace last 79 heats and another 318. Four furnaces in this plant did better than 250 heats per roof, while five furnaces approximated but 150 heats.

In making the 80 repairs to the 24 furnaces, the following brick were used:

Silica	2,520,126
Magnesite	98,773
Clay	547,739

The value of this brick is not the only element to consider. Lumber will cost from $12,000 to $15,000 annually. Bolts, castings and other finished material will total $15,000, and there will be a scrap allowance or credit of $5,000 for the discarded, worn out castings, etc. There is thus $25,000 worth of materials per annum required other than brick.

Labor for rebuilding the above furnace is as follows:

	Hours
Open hearth and common labor	170,000
Bricklayers	20,000
Carpenters	7,000
Boilermakers	4,000
Total	201,000
	2,500 per repair.

Overhead, based on labor, would enhance this figure materially.

The loss of production is serious. Fifteen days operation is lost per furnace per annum, these being natural gas furnaces. On producer gas-fired furnaces, the lost time would be 20 days. There being 24 furnaces in this plant, and 24 × 15 = 360, the situation is that one furnace in this plant is never at work. As the annual tonnage is 1,000,000 tons of steel, there is a dead loss of 40,000 tons of steel due to rebuilding, and the fact that the open hearth is not a permanent structure. There is lost tonnage due to waiting on materials, charging machine, bad bottom, etc., which totals 40,000 tons. An annual loss of 80,000 tons of steel valued at $25 a ton means a $2,000,000 loss. Better refractories would probably have saved $^1/_4$ of this, or $500,000.

Refractories for Powdered Coal

The performance of powdered coal is quite conclusive after a period of seven years' service in one plant. The condition of powdered coal fired furnaces after 100 heats was worse than the condition of similar furnaces oil fired after 287 heats. Incidentally, gas fired furnaces in this same plant suffered even less than the oil. In the powdered coal fired furnace, the refractories cut away, the slag pockets fill faster and the checkers become choked. The general overall condition cannot be entirely attributed to the ash that naturally is present in powdered coal. A coöperative study of this method of utilizing fuel must be made.

Open Hearth Furnace Design

Open hearth furnace design is far from uniform. Furnaces in different plants, and in some cases existing in the same plant, of the same rated capacity melting the same size heat will vary in width, length, volume of checkers, etc. These variations cause radically different velocities in the different parts of the furnaces.

The Carnegie Steel Company has adopted standard practices for open hearth. These standards are:

(1) Fuel: Producer Gas: Producers 2 per furnace, each producer to gasify 60,000 lbs. of coal per day, *i. e.*, the 2 gasify 5000 lbs. per hr.

(2) Capacity of Furnace: 100 tons; bath area 650 sq. ft. at the slag line.

(3) Bottom: Pan type, with 12″ sintered magnesite on 12″ magnesite brick on 24″ fire-clay brick.

(4) Roof: Body straight arched in one direction only with 24″ spring. Roof thickness to be 12″. Only standard shapes to be used.

(5) Doors and Frames: Water cooled, doors electrically operated.

(6) Buckstays: Slab type, water cooled.

(7) Front and Back Walls: Supported on water-cooled coolers at the slag line.

(8) Ports: Semi-water cooled type, cooled at vital points.

(9) Bulkhead: Water cooled.

(10) Air Regenerators: Minimum 68 cu. ft. per ton with minimum 150 square feet of surface per ton. 6,800 cu. ft. and 15,000 sq. ft. standard for 100 ton.

(11) Gas Regenerators: Minimum 46 cu. ft. per ton, with minimum 100 square feet of surface per ton. 4600 cu. ft. and 10,000 sq. ft. standard for 100 ton.

(12) Valves: Area of gas and air valves 10 sq. ft. each.

(13) Damper: Cast iron, inclined and air cooled.

(14) Stack: 6 ft. in diameter, 180 ft. high.

(15) Waste heat boilers to be considered as standard equipment.

With this standard in mind, it is interesting to compare other open hearth furnace dimensions. As the standard 100 ton furnace of the Carnegie Steel Company cannot be so taken for the entire industry, it is necessary to compare furnaces of different capacities. This is done in the following tables.

The lack of agreement in major dimensions causes each open hearth furnace installation to be a study unto itself. How seriously this affects the brickwork may be judged by considering the velocities encountered. In this case a set of eight open hearth furnaces whose standards approach that of the Carnegie Steel Company are taken to make the estimations.

Good steam engineering practice is to hold the velocity of steam in a pipe to a mile a minute, that is 5000 feet per minute, which is a gale of wind figured in ordinary standards at 60 miles per hour. Burning gases pass through various parts of an open hearth furnace at this velocity, cyclonic in speed, capable of carrying a substantial quantity of material in its current.

Producer gas weight .07111 per cu. ft., air .0765 and flue gases .0872. A 100 ton furnace utilizes 350,000 cu. ft. producer gas per hour, or 6000 cubic feet per minute. 1 cu. ft. producer gas requires 2.8 cu. ft. air and makes 3.5 cu. ft. flue gas. 1 lb. producer gas requires 3 lbs. air and makes 4.25 lbs. of flue gas, the addition to the flue gases representing leakage, etc.

The velocities through a 100-ton furnace approximate the following. A gas expands one volume for each increase of 500°F. Thus the 6000 cu.

TABLE I—COMPARISON OF DIMENSIONS OF OPEN HEARTHS OF DIFFERENT CAPACITIES

Capacity	200	100	60	50	40	20
Hearth length	40′0″	39′8″	36′0″	27′0″	34′0″	22′0″
Hearth width	14′6″	15′0″	13′6″	14′0″	13′0″	12′0″
Sq. ft./ton	2.9	3.9	8.1	7.5	11.0	13.2
Cu. ft. gas. reg.	5786	3912	1455	1122	1787	909
Cu. ft. / ton	28.9	26.1	24.3	22.4	44.7	45.4
Cu. ft. air reg.	7612	6685	1905	1870	2501	1187
Cu. ft./ton	38.1	44.5	31.8	37.4	62.5	59.3
Gas uptake	1800 s″	1296	960	1740	2658	576
Air uptake	3600 s″	2160	1566	2016	3294	702
Gas port	5.4 sf	3.1	6.6	9.0	2.9	2.0
Air port	15.8 sf	14.0	10.4	13.5	13.5	3.0
Gas valve	42″	42″	42″	42″	42″	27″
Air valve	48″	32″	48″	42″	48″	27″
Chimney	6′0″ × 130′	6′ × 120′	7′ × 140′	6′ × 150′	5′6″ × 140′	3′6″ × 120′

TABLE II—COMPARISON OF DIMENSIONS OF OPEN HEARTH FURNACES OF 50 TONS CAPACITY

Capacity	50	50	50	50	50
Length	32′0″	27′0″	34′0″	29′0″	31′0″
Width	13′0″	14′0″	12′8″	16′0″	13′0″
Sq. ft./ton	8.3	7.5	8.6	9.3	10
Gas regenerator	23 × 12 × 9	22 × 6 × 9	24 × 7 × 14	17 × 10 × 14	......
Cu. ft.	2397	1122	2401	2485	......
Air regenerator	35 × 12 × 9	22 × 10 × 9	24 × 11 × 14	17 × 12 × 14	12 × 12 × 14
Cu. ft.	3421	1870	3687	2979	2640
Gas reg. cf. ton	47	22	48	50	......
Air reg. cf. ton	68	37	73	59	66
Gas port area	9	......	7.6	......	4.5
Air port area	13.5	......	7.0	......	10.8

ft. of producer gas measured at 60°F, expands at 1100°F, two volumes, *viz.* 3 times 6000, or 18,000 cu. ft. at 1100°.

COMPARISON OF GAS VELOCITIES IN OPEN HEARTH

Part of furnace	Area sq. ft.	Temperature, Deg. F	Volume of gas, cu. ft.	Velocity, Feet per min.
Gas Valve	10	1100	18000	1800
Gas Entry Regenerator	30	1100	18000	600
Gas Regenerator Max.	157	2100	30000	200
Checkers Cross	97	2100	30000	310
Gas Take Off	20	2100	30000	1500
Gas Uptake	14	2100	30000	2200
Gas Port Top	8	2100	30000	3800
Gas Port Lip	6	2100	30000	5000
Air Valve	10	100	17000	1700
Air Entry Regenerator	47	100	17000	360
Air Regenerator Max.	257	2000	85000	330
Checkers Cross	162	2000	85000	520
Air Take Off	28	2000	85000	3000
Air Uptake (2)	25	2000	85000	3400
Air Port Top	42	2000	85000	2000

The flame temperature developed will approximate 4000°F. The 6000 cu. ft. of producer gas plus 17,000 cu. ft. air (total 23,000) expand to 9 times this volume, or 207,000 cu. ft.

The cross section of the hearth is 114 sq. ft., and an average velocity of 1750 feet per minute is attained. Friction of the walls and roof will cause counter currents, heat waves, and hot spot reflection from roof. Bath and walls cause interference. There is every probability that the gases in the hearth reach steam velocities that of 5000 feet per minute.

The 207,000 cu. ft. of gases at 4000 lose heat, contract and leave the hearth at approximately 3000°F, or slightly higher. A contraction to 150,000 cu. ft. seems reasonable, and it must pass through the gas and air ports on the opposite end of the furnace. In area the air represents 80%, hence 120,000 cu. ft. pass through it, and 30,000 cu. ft. through the gas port. The burned gases velocities then become:

Gas Port Lip	6	3000	30000	5000
Gas Port Top	8	3000	30000	3700
Gas Uptake	14	3000	30000	2100
Gas Take Off	20	3000	30000	1500
Gas Checkers	97	3000	30000	300
Gas Regenerator Max.	157	3000	30000	190
Air Port Lip	30	3000	120000	4000
Air Port Top	42	3000	120000	2800
Air Uptake	25	3000	120000	4800
Air Take Off	28	3000	120000	4300
Air Checkers	162	3000	120000	740
Air Checkers Max.	257	3000	120000	450

The gases are in some cases passed to a waste heat boiler but in the average case to the stack at 1000°. Flue gases being 3.5 times the volume of producer gas, mean 21,000 cu. ft. times 3 volumes for existing temperature or 63,000 cu. ft. per minute. The standard 6 foot stack, area 29 sq. ft., hence has gases passing through it at 2200 ft. per minute.

Due to the radical differences in design, proportioning of parts, etc., in open hearth furnaces, there will be different velocities encountered in each installation. Some are right, some are wrong; all cannot be right.

Enhancing the wear and tear of velocities are reversals. Water hammering in steam lines can break the pipe. The analogous effect in gas lines probably destroys brick. A quick closing of a valve in a high velocity water line will break the pipe. What is the effect of quick closing of open hearth valves on brickwork?

Approximately 500 reversals per week are the lot of an average open hearth. It seems impossible to regulate this operation mechanically, hence it is noted that the shortest period a regenerator may be on air or gas may be 2 minutes and the longest 70 minutes. The average may be 10 minutes, but the average time does not indicate the exact conditions.

An open-hearth furnace must melt and refine. This requires adjustment of temperature not recorded by a pyrometer. The latter is one of judgment and skill of the melter. On a two shift basis there are two first helpers. They are the melters. One takes the left hand end of a furnace, the other the right hand end. A bad end always develops. Jack favors his, and Jim his. What will happen on a three shift basis remains to be seen. In any event there is a human element present in which a bad end of a furnace gets worse, and reversals cannot be made a matter of mechanical refinement.

Little or no progress is being made in open hearth improvement, and the buck has been passed to the refractories man. He can take up the matter with profit to himself and to all concerned.

Velocities, reversals, a bad end, puff backs, minor explosions, scoring, slagging action, many enhanced by velocities seem to be the leads to follow on making better refractories.

The law of diminishing returns works on taxes. It also works on furnaces. A steam boiler operated at an overload furnishes steam at a marked economy in fuel. Carried to extremes a boiler is soon wrecked. The open hearth is also worked at an overload and at a marked saving in fuel. Thus a 50-ton furnace became a 60-, a 60- an 80-, and an 80- a 100-ton furnace. In many cases relatively few additions were made to get the larger capacity, and the overload shows itself in the brickwork. This is the situation viewed broadly. There is no reason why the experiences gained in operating at an overload should not be standardized. Who is going to do it?

Part of the procedure is the steel works initiative. Part of the procedure is the refractories manufacturers' initiative.

From 1880 to 1919, 14,281 boilers blew up, killing 10,000 people and injuring 17,000. The A. S. M. E. compiled a boiler code, and it has been adopted as law in 17 states. The results are apparent; accidents have been reduced. Overload caused these failures. Fortunately the open hearth does not blow up, but overload has caused increased expense, particularly in refractories.

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OPERATING CONDITIONS IN THE OPEN HEARTH AS THEY AFFECT REFRACTORIES[1]

By Clyde E. Williams[2]

In the open-hearth steel furnace, operating conditions and the life of refractories vary so much in different plants that it is dangerous to generalize and difficult to cover all phases of the problem. Acid and basic open-hearth furnaces differ mainly in hearth composition, that of the former being silica and of the latter magnesite. Acid practice is largely a melting operation and its refractory requirements are less severe than are those of basic practice. Moreover, less than 4% of the open-hearth steel produced in this country is made in the acid furnace. Hence, principal consideration will be given here to the basic open hearth.

Hearths

The hearth is subjected to severe action and must be repaired after every heat. Depressions and cracks are made during charging as a result both of the mechanical effect of the materials charged and of spalling due to changes in temperature. The siliceous hearth of the acid furnace is corroded during the melting stage by iron oxide formed by oxidation of the steel scrap and by that already present in the scrap. The banks are attacked by the slag, which, though siliceous, contains oxides of iron, manganese, and calcium. Acid open-hearth slags may contain 30 to 40% iron and manganese oxides and 2 or 3% lime.

The basic hearth is corroded by silica in the ore charged and by the slag, which, although strongly basic, contains sufficient silica to attack the magnesia lining. A typical basic slag contains 19% silica, 27% iron and manganese oxides, and 52% calcium and magnesium oxides; the iron oxide content may be higher at the beginning of the heat and lower at the end. In addition to the action of the slag, a strongly corrosive silicate of iron and calcium is formed on the silica front and back walls by the action of the basic oxides carried by the furnace gas. This slag runs down and eats into the hearth at its point of contact with the brick walls. Were it not for this action the hearth material could be carried further up the front and back walls than is now done, resulting in protection of the walls from corrosion. A wall built of a refractory that would resist the fluxing action of the oxides of iron and calcium contained in the gas would decrease the hearth repairs now required for silica walls.

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[2] Superintendent, Northwest Experiment Station (Seattle, Wash.), Bureau of Mines, Department of the Interior.

In repairing the basic hearth, calcined magnesite is placed in the larger depressions and either raw dolomite, calcined dolomite, or a prepared sintered dolomite containing iron oxide or ferruginous slag is added to the smaller holes. This operation requires much time and labor and also introduces to the furnace atmosphere basic oxides which may corrode the silica lining and help clog the checker work. In some plants an automatic machine using compressed air and a nozzle feeds the patching material where needed. A saving in time, labor and raw material is claimed, and, in addition, it is likely that, due to less dusting, a smaller amount of slagging substances is carried into the furnace atmosphere.

Walls, Roof, Ports and Bulkheads

Failure of the lining above the slag line is due principally to three effects: (1) fusion; (2) abrasion and slagging by the constituents of the furnace atmosphere, and (3) spalling and breaking.

Fusion of Lining

The temperature of the steel must be raised to about 2900–3000°F. The furnace lining is as hot and usually is much hotter, and a flame temperature higher by at least 200°F is used. The pressure in the walls is not large and in the silica roof the load is in the neighborhood of 12 to 18 lb. per sq. in., depending upon the size and design of the furnace. The proper design of ports to produce a flame that will neither strike the roof, the side walls, nor the opposite end is essential to prevent rapid destruction of the furnace. Even with suitable design, it often happens that the port, unless water-cooled, wears away unevenly and prevents suitable control of the flame, causing more rapid destruction of the furnace lining. Although water-cooled ports produce a lower flame temperature and decrease the thermal efficiency, their use is justified so long as the present refractories, which are working at practically their maximum possible temperature, are used. Sometimes, careless operators may allow the flame to travel the entire length of the furnace and impinge against the brick work at the opposite end with disastrous results.

The desire to increase the furnace output by increasing the flame temperature causes more rapid melting away of the lining. Increased refractory cost must be balanced against profit obtained by larger output. Insulation of the roof, walls, and uptakes will give lower fuel consumption but will increase refractory cost. About 16% of the heat supplied to the furnace is lost by radiation and convection from the combustion chamber and port ends, and about 7% from the checkers and uptakes.[1] Hence, the saving of even a small proportion of this heat would represent an important fuel economy, in view of the fact that only about 16% of the heat supplied is used in producing steel. It seems highly probable that better refractories than silica brick, even at considerably greater cost, can be used profitably to permit the use of higher temperatures and to save heat now lost.

Abrasion and Slagging

The stream of gas passing through the furnace carries with it small particles picked up from the bath. These particles are thrown against the interior of the furnace abrading it after the nature of a sand-blast. This action is particularly severe at points in the furnace where the flame is forced against the lining as a result of piling the charge unevenly in the furnace, and at the ends where the gas stream meets the ports and bulkheads directly. These solid particles not only attack the lining by their physical abrading action, but they also become impregnated in the brick and form easily fusible compounds, which, naturally, are more concentrated at the inner face where the temperature is greatest. Figures 1 and 2, containing photographs of two roof brick, show the degree to which impregnation has taken place. The chemical composition of the solid matter contained in the furnace atmosphere, as shown by analyses of various silica brick taken from roofs, sidewalls, bulkheads, downtakes, and checkers as well as the deposited material in slag pockets and regenerators, is largely iron oxide and calcium oxide. The ratio of these two substances varies in different furnaces and undoubtedly at different times in the same furnace; however, evidence gathered thus far indicates that iron oxide predominates. The ratios of iron oxide to calcium oxide in samples of silica brick have ranged from 2:1 to 5:1 and in samples of checker deposit from 5:1 to 10:1; this, in spite of the fact that the refining slags contained iron oxide and lime in the ratio of about 1:3. This slagging action by basic oxides is very important and points out the fundamental fallacy of using silica ware above the slag line in either the acid or basic open-hearth furnace.

The method by which these basic oxides are taken up by the gas stream, their chemical composition, and physical state are not known definitely. Undoubtedly, most of the iron oxide is introduced by the burning of light weight steel scrap during melting and by the oxidation of molten iron during the "boiling period" when the entire bath of metal and slag is being violently agitated. Thus, the hot oxidizing gases are intimately mixed with the metal and are afforded a fine opportunity to produce iron oxide and carry it away. Lime and other ingredients of the slag are also picked up by the furnace gases at this stage.

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[1] C. L. Kinney, Jr., and G. R. McDermott, "Thermal Efficiency and Heat Balance of an Open-Hearth Furnace," Yearbook, Am. Iron and Steel Inst. (1922).

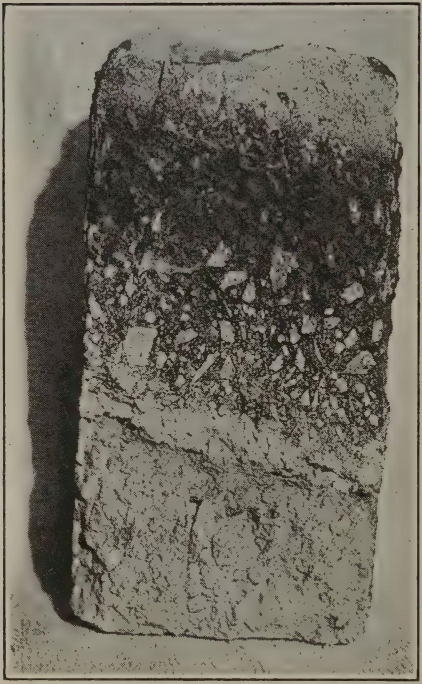

FIG. 1.—Cross-section of brick taken from roof of open hearth after 125 heats.

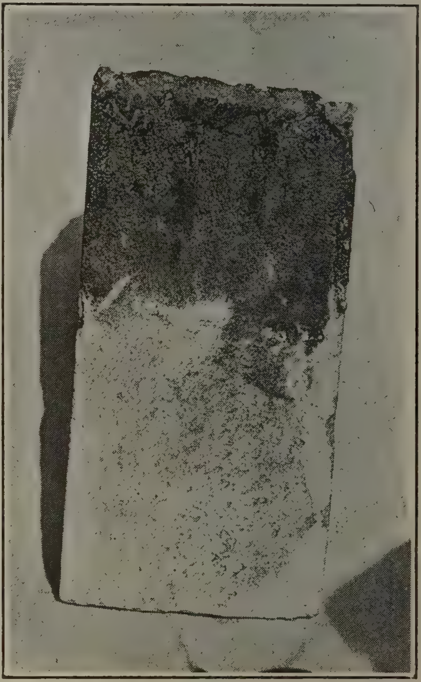

FIG. 2.—Side of brick taken from roof of open hearth after 30 heats.

Spalling and Breaking

New furnaces are brought up to operating temperature gradually and spalling is avoided as far as possible. However, brick used for patching hot furnaces are subjected to extremely rapid changes in temperature. Silica brick spall badly under such conditions. The use of hot silica brick for this work has proved advantageous in some cases. Chrome brick have given excellent service in patching hot furnaces. Silica brick in which the quartz has been converted to tridymite should be desirable for such use provided they could be produced cheaply enough. Silica brick in roofs are often cracked by excessive pressure at certain points caused by the brick having uneven surfaces. The lower portions of such brick drop out and the surrounding brick, with new sides freshly exposed, either spall or are rapidly corroded, producing a large weak spot in the roof which must soon be repaired.

Back walls are injured when rammed by the charging machine. This danger may be averted, or, at least, the extent of injury may be minimized by building into the brick work heavy iron bars which run horizontally across the wall.

Regenerators and Slag Pockets

Regenerators fail largely as a result of the deposition of dust coming from the open hearth. This dust gradually chokes the system and also forms a glazed surface on the brick by slagging the exposed face. Both actions cause inefficiency and ultimately make a cleaning out or rebuilding necessary. The rate at which steel is produced by the open-hearth furnace decreases as the checker work becomes clogged. Hence, the regenerators are cleaned and rebuilt, when, in the judgment of the operator, further use of them becomes uneconomical. Thus it is that the life of checker chambers varies in different plants using similar practice, some operators preferring a long checker life at the expense of diminished output.

The checker deposit consists of particles of iron oxide, lime, etc., carried from the bath, and also, in some cases, carbon and ash from the fuel burned. The analysis of a typical deposit of unfused material found in the checkers of a furnace burning oil and melting all steel-scrap charges follows: SiO_2, 10.2; FeO, 66.3; CaO, 4.9; MgO, 0.9; carbon, 0.07%. Some slag adhering to the brick contained SiO_2, 40.5; FeO, 27.0; CaO, 3.4; MgO, 0.2; carbon, 0.11%. Tar when burned in the open hearth sometimes causes the deposition of carbon in the checkers, and powdered coal may cause both coal-ash and carbon to be carried into the regenerators. Quigley[1] gives the following to show the effect of various kinds of fuels on the life of the checkers:

NUMBER OF HEATS BEFORE CLEANING CHECKERS

Natural or coke-oven gas	300–600
Coke-oven gas and tar	200–300
Oil or producer gas	200–300
Tar	175–250
Powdered coal	75–125

The usual size of the checker openings is of necessity a compromise between large and wide openings to prevent early clogging by dust, and small and narrow openings to get efficient transfer of heat. It is claimed that at one plant the deposition of dust is prevented to a large degree by maintaining a uniform rate of flow of gases through the checkers. This is accomplished by making the checker openings larger at the top than at the bottom and gradually reducing their area in stages going toward the bottom. Other designs make possible the periodic blowing of the chambers with air to remove deposited material. At another plant the brick are specially shaped so that no corners will project to catch dust particles suspended in the gas stream.

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[1] F. B. Quigley, "Open-Hearth Furnace Regenerators," Am. Iron and Steel Inst., Oct. 25 (1923).

Although much is to be gained in the better design of regenerators to prevent the deposition of solids, it seems more logical to remove these solids from the gas stream before it reaches the checkers. This is the purpose of the slag pockets but their performance is far from perfect. As the slag pocket becomes filled, the gases pass more directly to the regenerators and, as a result, less of the solid particles are removed from the gas stream before it enters the checkers. Methods for removing the slag periodically either by chilling and dropping out the granulated material or by keeping it molten and removing by tapping are helpful. The insertion of baffle walls causes a larger deposition of solids but the maintenance of these walls presents a difficult refractories problem itself.

Where sufficient room can be had, it may be advisable to construct a large chamber between the slag pockets and the checker work to permit a further deposition of entrained particles from the gases. Another possibility would be the electrical precipitation of the solid particles from the gases by some such method as is used in removing solids from lead and copper smelter gases; but on account of the high temperatures involved, present equipment and methods could not be used.

The highest temperature in the regenerators is at the top where the hot gases enter and is ordinarily between 2400 and 2600°F. Thus, the brick at the bottom are under the heaviest load and at a comparatively low temperature, whereas the brick at the top are at a high temperature and under the lowest load. Occasionally, checker brick are fused, but failure of regenerators due to this cause is not so important as that due to deposition of dust.

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FIRE-CLAY BRICK FOR THE OPEN HEARTH[1]

By M. C. Booze

ABSTRACT

Fire-clay brick in the open hearth are normally subjected to medium temperatures and to the action of slag containing high percentages of iron and lime. Temperatures near the maximum of the open hearth itself may exist due to failure to reverse the draft and for that reason brick of high refractoriness are used. Resistance to spalling

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[1] Presented at the Atlantic City Meeting, Feb., 1924 (Refractories Division).

action is not of primary importance because the temperature change is small. The indications obtained from a laboratory test were that brick having a high alumina content would resist the slag action better than ones higher in silica.

The use of fire-clay brick for open hearth furnaces is confined almost entirely to the regenerators. In this position they are subjected to the heat of the outgoing gases, to the slagging action of the dust carried by the waste gases and to temperature changes at frequent intervals.

Although the furnace itself may be operated at a temperature in the neighborhood of 3000°F, the waste gases entering the checker chambers are not in excess of 2600°F. This is due to the loss of heat to the walls of the flues leading to the checker chambers. The temperature, however, may approach the actual furnace temperature if for some reason the dampers are not reversed at the regular period. They are also dependent somewhat upon the construction and operation of the furnaces.

The following temperatures have been given for furnaces operated in various plants:

Plant	Temperature	Temperature drop during reversal
1	Air checkers 2600°F max. Gas checkers 2400°F max. Gases leaving checkers 1400°F max.	250°F–500°F
2	Air checkers 2350°F max. Gas checkers 2100°F max. Gases leaving checkers 1600°F	
3	2200°F max. Not stated whether in air or gas checkers.	200°F–300°F, where draft is reversed every 15 minutes.

It will be noted that in both cases where air and gas checker temperatures are given, the latter is the lower. This is partially due to the gases entering the flues leading to the gas checkers through a water cooled port. While the normal temperatures existing in either regenerator are not exceptionally high, the brick used must be of ample refractoriness to withstand the extreme temperatures which may prevail for short intervals due to some abnormal operating condition.

The temperature change taking place when the draft is reversed is rapid, but covers a narrow range and the minimum temperature is also high, so that the stresses tending to cause spalling are of little importance.

The height of the checker brick setting is rarely above 15 feet and since the checkers are set open in order to present a large heating surface, the load on the bottom brick would attain a maximum of not over six or seven pounds per square inch. The temperature at the bottom of the checkers, where the maximum load occurs, is comparatively low, so that little or no deformation or crushing would be expected even on brick having relatively low strength. The available data bear this out, it being stated that no failure from such cause has been observed.

The deposition of dust on the checkers eventually causes such clogging of the regenerator that the furnace must be shut down and the checkers cleaned. The number of heats between cleanings varies with different plants, but when producer gas is used it is considered that 300 heats is very satisfactory. When such cleanings are made, the top eight to twelve courses of brick are usually found to be so eroded and sintered together by slag that they cannot be salvaged. The lower courses, however, are less affected and may be used several times before they must be replaced. The explanation for this difference lies in the difference in temperature from the top to the bottom of the checkers, those at the top operating at 700–1000°F hotter than the lower ones. It is evident then that brick in the top rows of the checkers which did not slag readily would retard the clogging action and would increase the efficiency of the regenerator when measured over a long period. Silica and magnesite have been tried for this purpose, but neither was sufficiently successful to warrant continuance of the practice. One objection to silica brick is that a low percentage is salvable upon cleaning, due to breakage.

As has been stated, the temperatures in gas checkers are lower than those in the air checkers and for this reason if for no other the gas checkers are less slagged than the latter. There also is a carbon deposit made on the gas checkers which prevents to some extent the adherence of the slag. The volume of gases passing through the gas checkers is relatively smaller than through the air checkers and so less dust per unit of brick is carried in and deposited. Since the waste gases entering the gas checkers go through a port below the center of the passage to the air checkers, it is probable that the dust carried into the former would not have the same composition as that entering the latter. The following analyses bear this out:

	Slag from air checkers	Slag from gas checkers
Silica	16.69	24.53
Alumina	23.08	15.36
Iron Oxide	45.46	43.92
Lime	11.14	9.77
Magnesia	3.55	1.83
K_2O and Na_2O	1.57	3.90
Fusion point	Cone 8	Cone 6

A third analysis for such slag which has been obtained from a steel plant laboratory is as follows:

Silica	45.75	Lime	4.59
Alumina	4.84	Magnesia	3.44
Iron oxide	28.17	Carbon	0.08
Manganese dioxide	0.67		

It was not stated whether this came from the air or gas regenerator.

It has been the general practice to use first quality fire-clay brick in both regenerators. The experience of one steel plant has been that machine made brick give better service than hand-made, it being these peoples' belief that the resistance to slag action was greater, that the thermal efficiency was greater, and that they laid up better due to greater uniformity.

Using the two slags whose analyses were given previously, tests of four kinds of brick varying in silica content were made by determining the fusion point of cones made from mixtures containing 75% brick and 25% slag. The results obtained were as follows, using slag from gas checkers:

Brick sample no.	Silica	Alumina	Fusion point of slag-brick mixture
1	39.7	54.1	15–16
2	72.0	25.0	8
3	94.0	2.0	20
4	49.7	44.7	14–15

Fusion point of slag alone—Cone 5

Using slag from air checkers:

Brick sample no.	Silica	Alumina	Fusion point of slag-brick mixture
1	39.7	54.1	26–27
2	72.0	25.0	13
3	94.0	2.0	15
4	49.7	44.7	20–26

These results indicate but little advantage in the use of a highly aluminous material over good fire brick. It is probable that brick with a higher alumina content than those given as No. 1 would show less reduction in refractoriness, but the cost would be high for material of this quality.

The data presented here refer entirely to furnaces using producer gas as fuel and will not necessarily hold for other methods of heating. One writer states that the checkers must be cleaned every 75 to 125 heats when powdered coal is used, due to the coal ash being carried in, as compared with cleaning every 200 to 300 heats when oil or producer gas is used. In addition to the differences in the deposits, a variation in checker temperature would be expected with other kinds of fuel. The use of producer gas is common, but is being displaced to some extent by coke oven gas.

It has been indicated that fire-clay brick which will withstand a high temperature and which will not be rapidly eroded by slag will give good service in these regenerators. It has not been well established whether a dense or open brick has the higher thermal efficiency for this purpose and the latter problem should receive some attention.

Liberal use has been made of articles by Quigley "Open Hearth Furnace Regenerators,"[1] Kinney and McDermott, "Thermal Efficiency of the Open Hearth Furnace,"[1] and of data obtained from private correspondence with men acquainted with open hearth furnace operation. The only original data presented are those on analyses of slags taken from air and gas regenerators and on the results of fusion tests made with these slags.

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[1] American Iron and Steel Institute Meeting, October, 1923.

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CHROME REFRACTORIES FOR THE OPEN HEARTH[2]

By Raymond E. Griffith

ABSTRACT

This is not a technical paper but a compilation of notes on chrome ore, and the various forms in which it is used in open hearth furnaces, with a discussion of recent improvements in chrome brick that have permitted their broader use. Also some performance data secured through the courtesy of many companies and individuals operating open hearth furnaces.

Introduction

There is probably no other refractory used in the basic open hearth furnace that is of greater value, from a standpoint of utility or performance, than chrome ore; nor is there any other refractory material, the successful use of which, in many forms, is so rapidly increasing, and in such a variety of applications.

Chemists, metallurgists, engineers, in fact most everyone connected with the steel industry can claim a pretty thorough knowledge of the value and functions of chromium in metallurgy but it has been only in comparatively recent years that any serious study has been given the refractory qualities of chrome ore that would tend to broaden its application or encourage its more intelligent selection for refractory purposes. Nor has there, until recently, been much evidence of a desire on the part of the consumer to differentiate between good and bad chrome brick or ore. So long as the chromic oxide content was above a certain minimum, and sometimes maximum silica specified, the other elements, the form in which they were present, or their relation to spalling, refractoriness and the many other properties that affect performance, were apparently of no consequence to the consumer.

It is the writer's purpose to avoid, as much as possible, the technical side of the subject except to present results of some fusion and slag tests on chrome ores and chrome cements; also to mention certain observations on chrome brick reported by some investigators, which might be misinterpreted by consumers, or at least might be applied generally to all chrome refractories while the investigation may have been, as is usually the case, confined to one grade of chrome and presented without any qualifying statements as to its physical nature, frequently not mentioning its chemical composition.

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[1] Iron and Steel Institute, 1923.

[2] Presented at the Atlantic City Meeting, Feb., 1924 (Refractories Division).

Some chrome ores of very good chemical analysis are practically useless for brick making on account of their physical condition, being friable and of a sandy nature.

The hard, dense ores from Rhodesia, South Africa, that break up into sharp, irregular-shaped grains when ground, undoubtedly make better chrome brick than any of the more friable ores.

About 1920 ceramic engineers of E. J. Lavino and Company, and the writer, began a study of the chemical and physical characteristics of chrome ores from all known deposits of commercial importance; the primary object of this effort was to determine the various forms in which the different elements occur in the crude ore, and to observe their effect on the bond, physical strength, resistance to chemical reactions and spalling tendencies of chrome brick. Very interesting facts have resulted, certain phenomena cleared up and manufacturing difficulties eliminated; thus, through a better understanding and control of chemical and physical changes that take place during the burning process, chrome brick are now being produced possessing chemical and physical excellence not previously accredited to this type of refractory.

Refractoriness of Chrome-slag Mixtures[1]

(Extracts from tests made for E. J. Lavino and Company, by R. M. Howe, formerly Senior Fellow, Refractories Manufacturers Association Industrial Fellowship, Mellon Institute of Industrial Research, Pittsburgh, Pa., and Mark Sheppard, formerly Ceramic Engineer, E. J. Lavino and Company.)

The following results were obtained by fusion tests to determine the resistance of chrome ore and chrome cements to slags as well as high temperatures.

Test A.—Actual fusion point of "Imperial" chrome ore without addition of slag was not definitely determined, but a fusion point above cone 38 was demonstrated.

Test B.—Straight "Imperial" chrome ore and four grades of specially prepared chrome cement each mixed with 10% acid open hearth slag were rigid at cone 34.

Test C.—Four grades of special cement each mixed with 20% acid open hearth slag were just beginning to react at cone 34. Straight "Imperial" ore and 20% acid slag was not affected, at cone 34.

Test D.—The same materials, each mixed with 20% basic open hearth slag all remained firm at cone 34.

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[1] These additions reduced chromic oxide content in mix to about 40%.

Effect of Impurities in Chrome Ore[1]

Following results obtained by adding to the natural "Imperial" ore 20% each of silica, iron, alumina and magnesia.

Test no.	Approximate total impurity in mix	Fusion point
1 Silica	25.84%	Cone $27^1/_2$
2 Iron Oxide	30.80%	Cone 33
3 Alumina	31.77%	Vitrified at Cone 33
4 Magnesia	31.36%	Unaffected at cone 33

It seems obvious, from this test that the elements which reduce the refractoriness of chrome ore are, in the order of their importance as fluxes, silica, iron oxide, alumina and magnesia. The last, however, having only slight effect on the fusion point of chrome ore. The practice is fairly common to mix dead burned magnesite with chrome ore, sometimes in equal proportions, for patching bottoms and many other parts of basic open hearth furnaces.

Properties of Chrome Brick

The general properties of chrome brick as reported by various observers, compiled by McDowell and Robertson and together with other valuable data, are most ably presented under the subject "Chrome Refractories."[2] Engineers, chemists, metallurgists and others interested in the subject will find this valuable contribution interesting and profitable reading. However, certain statements regarding spalling tendencies and physical weakness under load at high temperatures, to which many consumers are inclined to attach undue importance, might be modified to conform more closely with recent performance in the laboratory and in actual practice, of brick made in commercial quantities from ore analyzing 47 to 51% Cr_2O_3, ore selected with regard to its physical as well as chemical adaptability.

CHEMICAL ANALYSES

	Sample No. 1 Per cent	Sample No. 2 Per cent	Average Per cent
Cr_2O_3	50.00	49.72	49.86
SiO_2	7.42	4.78	6.10
Fe_2O_3	17.54	17.22	17.38
Al_2O_3	11.50	14.01	12.76
MgO	12.66	12.31	12.49
CaO	0.00	0.00	0.00

Each of these samples was composed of spalls from 50 brick. The two analyses represent the product of four different kilns, samples 1 and 2 made from slightly different ores, chemically, but possessing about the same physical characteristics.

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[1] These additions reduced chromic oxide content in mix to about 40%.

[2] *Jour. Amer. Ceram. Soc.*, **5** [12], 865–87 (1922).

Crushing Strength

Many times in the last two years these brick have been subjected to the standard load test and in every instance except some experimental mixes, the point of failure was between 1430° and 1470°C. While the load test as now employed is not, in the writer's opinion, at all representative of furnace conditions, but suitable only for comparisons, many furnace builders and operators are influenced in their selection of refractories by results obtained in this as well as other irrelevant tests; therefore, it may serve some good purpose to compare this behavior of chrome brick with some of the other commonly known refractories.

Fire-clay brick and bauxite brick, in the standard load test soften at about 1300°C. Magnesia brick frequently shears at 1400° to 1500°C. (sometimes as high as 1550°C). Silica brick shears at about 1600° to 1650°C. It is obvious that, of the small group of refractories suitable for metallurgical furnaces, chrome, so far as crushing strength is concerned, is better than fire clay or bauxite and about equal to magnesia brick.

Sensitiveness to Temperature Changes

The best evidence that considerable progress has been made toward reducing if not eliminating the spalling tendencies of chrome brick is the fact that many plants now use them for all hot repairs to front walls, back walls and other parts of open hearth furnaces; they stand temperature changes much better than magnesia or silica brick.

Chrome Brick in the Open Hearth

It is doubtful if, prior to 1916, it would have been possible to find a basic open hearth furnace in America with a complete chrome brick bottom. During the war there were a few cases where chrome were used in the place of magnesia brick, but because the latter were not immediately available and the demand for steel was so great that such apparent disregard for precedent was entirely permissible; however, since the latter part of 1920 improvements in the quality, and favorable market conditions have influenced consumers to take a more serious interest in chrome brick. In the last two years chrome brick have been used for the entire bottom and at the base of front and back walls, up to a safe distance above the slag line, in at least eighteen basic open hearths. Sixteen open hearth plants, with a total of 232 furnaces have adopted chrome as the most desirable brick for bottoms and many other parts of basic furnaces, replacing magnesia and in some places silica brick.

Specific Applications with Performance Data

While much of the following is apart from the main subject it will undoubtedly prove interesting to operating men. The writer made a personal investigation in a number of plants to secure first-hand information, some of which is of a nature that might be considered confidential therefore the source is designated by number only.

PLANT NO. 1

All open hearth furnaces basic (75-ton capacity).

Fuel.—Producer gas (average about 580 pounds coal per ton of steel).

Bottoms.—Last two rebuilt with chrome brick (two flat courses and one rowlock). All new bottoms are made with dead burned magnesite burned in on top of chrome brick. For all ordinary patching dolomite, calcined in their own cupolas is used. Use very small amount of grain magnesite for bottom repairs, about one half pound per ton of steel. Average consumption of dolomite charging 50% hot metal, is 60 to 70 pounds per ton. Charging 65% hot metal, dolomite consumption is usually 80 to 85 pounds per ton of steel.

Walls.—(Front and back.) Chrome brick at base; silica brick above slag line. Siliceous slag from silica walls seems to build up on chrome brick while it will cut out magnesia brick.

End blocks and monkey walls.—Built of selected lumps of "Imperial" chrome ore.

Ports.—Water cooled, paved with silica brick, faced or protected with ground chrome ore.

Bulkheads.—
Gas—silica brick
Air—silica brick
Run 35 to 40 heats without patching.

Roof.—12-inch silica, average life, new roof is about 190 heats before patching; with care in heating up and proper repairs, total life of center section (from knuckle to knuckle) is 250 to 300 heats.

Remarks.—Operating men in this plant expressed the opinion that crude ore, in the form of hard, dense lumps is the most economical and serviceable refractory available for use in monkey walls and end blocks. The service life is greater than other materials, also much higher salvage.

After more than two years experience, replacing magnesia brick with chrome they have found no apparent difference in the bottom but where they are exposed to temperature changes or come in contact with the drip from the silica walls, the evidence is strongly in favor of chrome brick.

PLANT NO. 2

Furnaces all basic (80 tons capacity).

Fuel.—Producer gas. Best furnace on producer gas averaged for the month, 480 pounds coal per ton of steel. Total production for the month 6000 tons steel.

This record made by an eighty ton basic furnace of special design which permits better direction of the flame, also more intimate mixture of gas and air. An incident in connection with this new furnace is a reduction in the steam pressure at the producer from 35 to 40 pounds down to 12 to 15 pounds. Regular 80-ton furnace, same plant, produced 5000 tons steel. Coal consumption 680 pounds per ton.

Bottoms.—One complete chrome brick bottom.

Walls.—(Front and back) now using chrome brick at the base of front and back walls in all furnaces. Silica brick above slag zone.

End blocks.—Lump chrome ore.

Monkey walls.—Patented magnesite brick in some furnaces, lump chrome ore in others. Service life is about the same, but first cost of lump ore is a great deal less with higher salvage value.

Ports.—Water cooled; use ground chrome ore for protecting floor of ports. In special furnaces previously mentioned the port arches form mixing chambers for gas and air. Extremely high temperatures are easily attained at this point. Selected lumps of chrome ore, bonded with "Kromepatch" are used for constructing these arches; all other refractories they have tried so far have failed to give satisfactory service. The contour of the arch or mixing chamber is maintained by a nest of water cooled pipes imbedded in the refractory and which also help to support it.

Bulkheads.—(Gas and air.) Silica brick, usual life 40 to 45 heats.

Roofs.—12-inch silica. Average life 200 to 250 heats.

Remarks.—Men in this plant expressed a preference for chrome brick. Said they would not hesitate to use chrome any place in an open hearth furnace where magnesia brick can be used.

PLANT NO. 3

All basic open hearth furnaces, 100 tons rating. Melting 130 tons per heat.

Fuel.—Producer gas. Average 508 lbs. coal per ton of steel, 30% hot metal.

Bottoms.—Has not been necessary to rebuild any bottoms since the plant began operations. Have adopted chrome brick for all future bottom repairs and construction.

Walls.—(Front and back) chrome brick at base; silica above slag line.

End blocks.—Lump chrome ore.

Ports.—Water cooled; paved with silica brick faced or protected with ground chrome ore.

Bulkheads.—Silica brick; frequently necessary to replace after 10 to 15 heats.

Roof.—12-inch silica, average life 250 heats.

Remarks.—Men consider chrome brick, equal to magnesite in every respect.

PLANT NO. 4

Basic open hearth furnaces, rated at 60 tons, melting about 83 tons per heat.

Fuel.—Producer gas, average coal consumption 600 lbs. per ton of steel, charging 50 to 55% hot metal. Operate new or rebuilt furnaces 100 to 150 heats on producer gas, then change to coke oven gas and tar.

Bottoms.—Most of the furnaces have the original bottoms still in service; however, contemplate using chrome brick for all new or rebuilt bottoms.

Walls.—(Front and back) have been experimenting for some time with lump chrome ore back walls; have had as high as 9 chrome ore back walls in operation at one time. These walls are usually 22 to 26 inches at the bottom tapering back to 13 to 18 inches thick at the top. It is now the practice to use four courses of chrome brick at the top of the wall.

To reinforce the back wall $1^3/_4''$ or 2-inch square bars, about 12 inches apart run the full length of the wall imbedded in the outside face.

Complete front wall recently installed, using selected chrome ore lumps. At time of inspection this front wall had run 103 heats; in excellent condition except two red spots near the skew-back.

One important advantage, in addition to the much greater life of these chrome ore walls compared with silica, is the fact that, contrary to the silica wall, the chrome wall wears away at the top instead of the bottom. With minor repairs along the top of the wall this type of construction lasts the full run of the furnace, frequently running 150 heats without any repairs.

End blocks.—Built of selected lumps of chrome ore. Usual life about 700 heats frequently lasting much longer.

Remarks.—Although the use of lump chrome ore (front and back) walls in this plant might still be considered in the experimental stage the results obtained have been encouraging and with further refinement in construction details will no doubt be adopted as standard practice and prove very economical.

PLANT NO. 5

Basic open hearth furnaces, rated at 100 tons, melting 120 tons.

Fuel.—Oil.

Bottoms.—Use chrome brick for all repairs and rebuilding.

Walls.—(Front and back) chrome brick all the way up to within a few courses of the skew-back, topped off with silica brick.

Furnace A—Chrome brick in back and front walls, air port bulkheads and end blocks. Furnace recently repaired using about 9000 chrome brick after run of 271 heats.

Furnace B—Recently repaired using 9000 chrome brick, previous run 280 heats.

Furnace C—After 90 days run, over 200 heats, this furnace was in good condition; front and back wall appeared to be good for another 100 heats.

Furnace D—Given a general overhaul and put in service October 15th; on January 30th still in service after 236 heats. Do not expect to take this furnace off for another month which will give it a total run approximating 300 heats.

Furnace E—Taken off for repairs after 295 heats.

Remarks.—Chrome brick were used in the back wall in each furnace mentioned and chrome brick front walls in some of them.

In all these cases chrome brick bulkheads, and uptakes faced with chrome brick, have lasted the full run of the furnace.

Silica brick in these bulkheads would give in this plant about 20 days' service, about 45 to 50 heats. In back walls the life of silica brick is about 45 to 60 heats.

PLANT NO. 6

Basic open hearth furnaces, some 100 tons, others 70 tons capacity.

Fuel.—Producer gas, also one furnace on oil. Coal consumption, producer gas furnaces 675 lbs. per ton of steel; charging all cold metal. Oil-fired furnace, consumption fuel 44 to 45 gallons oil per ton of steel.

This plant runs extremely hot heats, tapping at approximately 2950°F, compared with 2700 to 2800 in ordinary practice. On account of charging cold metal and high heat required, it is considered good practice to get a 100-ton melt in 12 hours.

Bottoms.—Have not, so far, used chrome brick in the main bottom but they are considered suitable for this work and will no doubt be used for future rebuilding.

Walls.—(Front and back) chrome brick used at base of wall running up to about 5 courses above door sill, silica above this point. Silica walls usually repaired after 20 to 30 heats.

End blocks.—Faced with chrome brick.

Ports.—Some water cooled, others built of silica brick protected with ground chrome ore or "Kromepatch." Prefer the latter as it gives 2 to 3 times the service of regular ground chrome ore. This longer service is due to the fact that straight ground chrome ore does not develop sufficient bond to hold it in place at the lower temperatures, therefore most of it falls off long before the bonding temperature is reached.

Bulkheads.—(Gas) patented magnesite brick. Wall $13^1/_2$ inches thick. Experimenting with chrome brick. (Air) silica brick.

Roof.—12-inch silica; usually runs about 125 heats, then after general repairs gives about 125 to 130 heats more; some roofs have given as high as 300 heats which is considered a very good run in this plant.

Remarks.—Very well pleased with service rendered by chrome brick in all parts of the furnace where magnesia brick were formally used. Also use about 18 inches of chrome brick at the base of walls in soaking pits.

PLANT NO. 7

Basic open hearth furnaces, running 63 tons per heat; average heat 9 hours.

Fuel.—Producer gas; coal consumption 580 lbs. per ton of steel, 45% hot metal. With a new furnace, clean checkers, properly shaped ports, tight valves, and other factors effecting economy favorably they have produced steel for a short period with a coal consumption of 450 lbs. per ton.

Bottoms.—One complete bottom chrome brick; and they have also been adopted for all future bottom repairs and rebuilding.

Walls.—(Front and back) chrome brick at the base, silica above slag zone.

End blocks and monkey walls.—Faced with chrome brick.

Ports.—Water cooled; gas uptakes faced with chrome brick above hearth level.

Bulkheads.—Silica, 20 to 25 heats average life.

Roof.—12-inch silica, 250 to 300 heats.

Remarks.—Also use chrome brick in soaking pits, 7 courses at the base of the walls. Very well satisfied with service obtained from chrome brick they prefer chrome brick in the soaking pits and consider them fully equal to magnesia brick in the open hearth.

Conclusions

Many failures of the high grade ground chrome ores in the open hearth are, contrary to the general belief, due to their high refractoriness and difficulty of bonding at the lower temperatures.

Synthetic chrome cements, intelligently prepared, composed of high grade chrome ore, finely ground and intimately mixed with slightly less refractory but very plastic materials, so proportioned as to give the desired plasticity, strength of bond and adhesiveness without an appreciable sacrifice of refractoriness give much longer service (often lasting three times as long) hence, greater economy, than any straight ground chrome ore for patching and protecting front walls, back walls, port arches, inclines, end blocks, uptakes, door jambs, etc. In most cases where straight ground ore is used more than half the ore applied to a furnace wall falls off long before it gets hot enough to bond together or stick to the brick work.

Walls, end blocks and other structures built of crude chrome ore lumps would be more rigid and monolithic, with greater resistance to impact, corrosion, abrasion and other destructive forces if the uneven blocks were laid in a synthetic chrome cement composed of materials that would give maximum binding strength with the least possible decrease in refractoriness.

Chrome ore has remarkable resistance to the fluxing action of acid or basic slags and all chemical reactions encountered in the open hearth furnace. Its neutral characteristics and high refractoriness give it a broader field of usefulness than most other refractories. Synthetic cements made of high grade chrome ore are now used for laying magnesia, chrome, silica, fire clay and other types of brick.

High-grade chrome brick have proven fully equal to magnesia brick in basic open hearth bottoms and superior to magnesia or silica brick in bulkheads, gas and air uptakes, back walls, front walls and other places where conditions are most severe. Even a properly designed chrome brick roof is within the realm of possibilities which would permit longer runs between rebuilds, greater output per furnace and consequently lower cost per unit of output.

The remarkable increase in the use of chrome refractories made possible by improvements which, compared with probable future developments may seem insignificant, causes the writer to suggest that research and a study of service conditions, looking toward the improvement and more intelligent use of chrome, magnesite, silica, fire clay and other well known refractories is likely to give consumers more immediate and economical relief from their various refractory troubles than the development of super-refractories at costs which seem prohibitive and so far have discouraged their use in the open hearth and most other ordinary types of furnaces.

PHILADELPHIA, PA.

ROOF BRICK FOR THE OPEN HEARTH[1]

BY H. C. HARRISON[2]

ABSTRACT

The conditions under which a roof brick has to stand are considered and possible means of improving refractories in common use suggested. A brief mention is made of the possibility of utilizing other available refractories.

Introduction

Open hearth operators have about reached the limit of economy in steel making until they can employ higher hearth temperatures. In order to permit of this improved operating condition, the steel men must either be furnished with better refractories or else the refractory materials now in use must be utilized to better advantage.

In order to open the question of roof brick, let us first consider the conditions under which a roof brick has to stand and, second, suggest methods for realizing a greater service from the refractories now in common use. The third point will have to do with what has been done in the way of improving the refractories in common use; and lastly, the possibility of utilizing other available refractories.

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[1] Published by permission of the Director, U. S. Bureau of Mines. Presented at the Atlantic City Meeting, Feb., 1924 (Refractories Division).

[2] Assistant Metallurgical Engineer, Ceramic Station, U. S. Bur. of Mines, Columbus, Ohio.

Even with the great variation in design, fuel, and operating conditions in the open hearth furnace, it still remains that the life of the furnace is limited by the life of the refractories used in the various parts. In all cases, the refractory in the roof of the open hearth if not the limiting factor, is one to be seriously considered.

In basic open hearth practice the life of the roof, with minor repairs, ranges from 80 to 350 heats, as found by a survey of furnace operating conditions. A high average life of the roof in basic practice is about 250 heats, while in acid practice on the average it is 700 to 800 heats. The ultimate failure of the roof is caused by the drip fluxing away the bricks until the roof will no longer support itself. The point of greatest attack in many cases is reported to be near the skew-back of the back wall opposite the middle door. The draft from the door tends to roll the flame up to the roof causing a local heating.

Operating Conditions

The operating conditions under which the roof brick are required to stand are not known with certainty. The temperature of the hot face is not definitely known nor are the gases near the roof known to be always oxidizing, although they are assumed to be such. The amount of suspended material in the gases in contact with the roof has not been determined. The character of the slag material coming in contact with the roof has never been shown to be the same as that in the bath, although this has been assumed in slagging tests.

Temperature near Roof The temperature to which the interior of an open hearth furnace near the roof is subjected in present practice, is probably between 3000 and 3200°F. The practice of the operator in general is to drive the furnace until the roof brick begin to drop or at least show a very decided tendency to do so; that is, the refractory in the roof is the indicator for the maximum working temperatures.

Load Conditions The load carrying characteristics of a roof brick at temperatures very close to its softening point is an all important consideration in furnace design where the roof is self-supporting, as in general practice. Even though the material had all the other characteristics of an ideal refractory, it would be of no use if it lacked ample strength to support the roof load at service temperatures.

Slag Conditions Slag action is an important factor in the ultimate failure of open-hearth roof-brick. The brick in service must resist the action of a basic fog, possibly carrying some very fine slag spray, in an atmosphere which is probably oxidizing at a temperature very near to their softening point. The basic fog referred to is composed of vaporized metallic oxides from the hot bath as well as dust from the charging. In basic practice the oxides of iron and lime predominate and in acid practice, the oxides of iron. The chemical nature of any fine slag spray that might be carried to the roof is, of course, dependent upon the process being used. An analysis of the drip from a basic open hearth furnace using a silica roof showed it to consist principally of iron oxides together with considerable amounts of silica and lime. The above consideration seems to indicate that a neutral or slightly basic roof would be the most desirable in both acid and basic open hearth practice since in both, the roof is subjected to a basically charged atmosphere.

The greater length of life of a silica roof in acid practice, it being practically three times the life of a silica roof in basic practice, is due to the somewhat lower temperature possible in the acid process since no refining of the steel is accomplished.

Abrasion Conditions Abrasion is the least important of the factors leading to the ultimate failure of an open hearth roof. The requirements of the steel making process are such that the flame must impinge upon the bath. Furnaces in general are constructed so that the air port is above the gas port thus tending to cause a blanket of air next to the roof. The only time the flame plays along the roof is at times of minimum kinetic energy so that only the smaller suspended particles can reach the roof. Since these small particles must be in a very plastic state at the flame temperature, their abrasive action will be very small and at the same time there will be a tendency to cling to the roof, so that slag action and increased temperature due to the flame contact must be far more important than any abrasion that might take place.

During a survey of furnace conditions, some operators were found to be of the opinion that the roof was exposed to the most severe conditions when the bath was quiet and the surface inactive. The roof was assumed to be thus overheated by the smooth glassy surface of the slag acting to reflect the heat up to the roof. Another operator found the most severe conditions encountered when the bath was very active, probably due to the flame thus being deflected to the roof. In this case slag action might be a serious factor due to an increased amount of spray being carried to the roof. The later operator found the composition of the charge seemed to have a definite effect on the life of the refractories.

Taking all factors into account, the ideal roof brick must have exact size and shape. The chemical nature of the material should be such that it will not flux readily with the slag with which the surface is covered—as above shown this means that it should be neutral or basic in nature. The brick must stand under working conditions with the hot face exposed to a temperature very close to its softening point. The porosity of the brick must be as low as is compatible with a low spalling value so that it will not absorb fluxes, which will lower its softening point. Finally the higher the softening point of the brick, the more nearly ideal it will be.

Thermal Conductivity Several writers have pointed out that the thermal conductivity of the roof brick is an important factor in determining the maximum working temperature they will withstand, since it is this property which determines the rate at which heat is removed from the hot surface of the brick. Hull[1] has shown in this connection that the need of more reliable and usable data on thermal conductivity of refractories must be emphasized, especially the need of data on thermal conductivity of commercial refractories in fabricated combinations. A point that detracts from the utility of available data on thermal conductivity of refractories is that the determinations are made on small or special shapes of questionable similarity to commercial brick while the values are intended for use on bricks in fabricated combinations. Beecher[2] has recently published values for the conductivity of silica brick at a fraction of previous values and below that of fire clay, while previous work has placed the silica in some instances above the fire clay, also, it is a generally accepted fact by furnace men that silica will transfer more heat than fire clay.

The most desirable combinations of refractoriness and thermal conductivity cannot be stated until more is known of the thermal conductivity of furnace settings. One operator stated the very decided opinion that he could raise the over-all efficiency of his furnace if given a roof brick of greater refractoriness, due to the possible utilization of a higher flame temperature, even though the new refractory had a decidedly greater thermal conductivity than silica brick.

Utilization of Refractories

Suspended Roof The importance of the load carrying characteristics of the brick at high temperature could be reduced by designing the furnace with a suspended roof. Such a roof is being tested in at least one installation at the present time. The advantages of the suspended type of roof are obvious, in that the load carrying requirements of the brick are reduced to their own weight suspended from the cool side and the decided advantage of being able to replace sections of the roof which receive the greatest wear, thereby obtaining a maximum service from other parts of the roof. Another feature of the suspended roof is the possibility of suspending the bricks from a water cooled support thus increasing the life of the roof. It is true that in general, water cooling is undesirable around a furnace but cooling of the roof would be far less objectionable from an operating view-point than cooling the gas ports and the gain would very probably off-set the disadvantages. The cooling should only be sufficient to make the refractories stand up under the increased temperatures. Any cooling above this amount only increases the loss. In a number of cases where cooling is practiced, needless losses are incurred through excessive cooling.

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[1] Walter A. Hull, "Refractories in the Steel Plant," Year Book of the Amer. Iron and Steel Institute, p. 470 (1921).

[2] "Studies on Thermal Conductivities of Some Refractory Materials," *Jour. Amer. Ceram. Soc.*, **7** [1], 19 (1924).

Silica Brick as Roof Refractory

At the present time practically all open hearth furnace roofs are built of silica brick. The abundance and cheapness of siliceous material and its method of manufacture and its desirable properties make it an economical material. It, at the same time, has the disadvantage that it will not permit of a more advanced hearth temperature. Several other materials have been tried as roof brick but have not been able to compete with silica.

The properties of silica brick are a fairly high refractoriness; strength and resistance to abrasion while hot; high thermal expansion; and sensitiveness to rapid temperature changes below a dull red heat. These brick are especially adapted to roof construction because of their lightness and rigidity under load at high temperatures. Together with their desirable properties, silica brick have the undesirable properties of tending to spall and of being decidedly acid in character although they must serve in a basically charged atmosphere at high temperatures.

The Mineral Form of SiO_2 in Brick Is Important

Based on the exhaustive researches of Fenner[1] much technical information on the firing of silica refractories has been worked out. Silica may exist in brick in three mineral forms, namely—quartz, tridymite and cristobalite. In brick intended for open hearth roof construction, tridymite is the most desirable form. In commercial brick, about 80% of the quartz is inverted but only a few per cent of this is present as tridymite, the large majority is in the form of cristobalite. Brick which have been in service through the life of a roof, upon examination show that back of the fused surface practically all the silica is in the form of tridymite.

J. S. McDowell[2] has stated the desirable properties of tridymite as;

1. "Tridymite has the least thermal or temporary expansion of the three silica minerals."

2. "Tridymite has the greatest specific volume of the three minerals and cannot show any permanent expansion after repeated burning below its melting point."

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[1] C. N. Fenner, "Stability Relations of the Silica Minerals," *Amer. Jour. of Science,* **36,** 383 (1913).

[2] J. Spotts McDowell, "A Study of the Silica Refractories," *Trans. Amer. Inst. Mining Engr.,* **57,** 3 (1917).

3. "A tridymite brick could probably be subjected to fairly rapid changes of temperature with little danger of cracking."

How to Convert SiO_2 to Tridymite

As indicated by McDowell's work, in the present method of manufacturing silica brick the time element appears to be the most important factor in the formation of tridymite. In the firing of silica refractories the maximum temperature is maintained about 40 hours in usual practice If the maximum temperature, providing it is under 2678°F were maintained for $2^1/_2$ weeks, a brick consisting almost wholly of tridymite could probably be formed. The impracticability of producing a tridymite brick by this method is obvious.

C. L. Kinney[1] built the regenerators of an open hearth of silica brick which were removed after one campaign. It was found that the brick so treated upon being built into the back wall of the furnace, gave twice the life of ordinary commercial brick. This lengthened life was probably caused by the better development of tridymite during the extended firing in the regenerators.

Another possibility of producing a tridymite brick lies in using another flux either in addition to or in place of the lime now used. This flux must have a more active catalytic effect upon the inversion to tridymite than lime and at the same time must not lower the softening point of the brick to any appreciable extent.

Rebuffat,[2] upon investigating the properties of a quartzite that showed a high rate of inversion to the lower density minerals, found a small per cent of phosphorous present. He then added a small per cent of this element to a quartzite which was free of this flux. The presence of the phosphorous considerably increased the rate of inversion of the quartzite upon heating.

In nature the most active mineralizers are the hydroxyl group, boron, and fluorine. The temperatures at which silica brick are fired exclude the consideration of the hydroxyl group. At the present time, investigations are being made into the possibility of producing a commercial tridymite brick by the use of one or a combination of the above catalyzers.

The possibility of a tridymite brick suggests the possibility of a silica brick of greater density due to the lower spalling tendencies of tridymite. A brick of lower absorption is very desirable. The open hearth operator has found that he can obtain the greatest service from his roof brick by glazing the surface. His practice is to heat the new roof at the first melt so that tiny droplets form on the surface. If he is unfortunate and more than glazes the surface at any point, this point will be more easily fused than any other during the following melts. This effect is probably caused by an absorption of impurities by the porous brick which effect could be reduced by producing a denser brick.

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[1] C. L. Kinney, Jr., Discussion of "Refractories in the Steel Plant," Yearbook of Amer. Iron & Steel Inst., p. 511 (1921).

[2] O. Rebuffat, "Dinas Bricks of Constant Volume—Preliminary Note," *Trans. Ceram. Soc.*, **21,** 66 (1921–22).

Other Means of Improving Silica Brick

It[1] has been suggested that improvement may be expected from a more careful preparation of the raw material—more especially in regard to sizing and mixing. It also seems that a study of machine molding under increased pressures might be worth while. As these factors would have some influence upon the physical strength of the ware as well as upon the rate of inversion, improvements could possibly be effected. Whether the added cost would be justifiable would depend upon the product.

In all that has been said, it will be noted that no suggestion has been made as to how the refractory value of silica brick can be raised. The amount of lime necessary to give the ware the necessary dry bond has been reduced to the minimum. In most cases very pure raw materials are used, so little improvement is possible in the way of raising the actual softening point of the ware. This feature is an inherent limitation in silica ware and if greater refractoriness is important, other materials must be considered.

Other Roof Materials

Experimental open hearth roofs of carborundum, bauxite, and chromite have been reported. Sillimanite and spinel are being experimented with at the present time in back walls with the idea in view of adopting them to roof service.

So far, none of these materials have proven as satisfactory as silica in spite of the fact that they are, without exception, more refractory and less acid in character than silica. The causes of failure of the three full roofs above mentioned are reported to have been mechanical rather than service failures.

The case of the carborundum roof installation is interesting in that it shows a possible treatment of a material combining high thermal conductivity and high refractoriness to prevent excessive heat losses. In this case the carborundum was built in as an ordinary roof, then an insulating crown of fire brick was built above the carborundum with a 2-inch air space between the two crowns.

If the suspension principle of roof construction ever becomes popular, it is likely that some changes will be introduced in roof materials as several of the above mentioned materials have more to gain by suspension than has silica. Magnesite and chrome especially come in this class since they have the advantage of high fusion points but will not sustain load at high temperatures. Along this same line it will be well to mention that one concern is at present figuring on building an all chrome furnace. It is very likely however that silica, due to its low selling price, will always be in demand except where exceptionally high hearth temperatures are desired.

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[1] E. E. Ayars, "How Good Silica Brick Are Made," *Brick and Clay Record*, Oct. 30, 628, and Nov. 13, 698 (1923).

COLUMBUS, OHIO

SOME CONSIDERATIONS NECESSARY IN SELECTION OF REFRACTORIES FOR THE OPEN HEARTH[1]

A SYMPOSIUM CONDUCTED BY D. A. LYON

MR. CORNELL: Mr. Crosby stated the life of an electric furnace in pounds. I would like to know what they consider satisfactory for their furnaces on heats, not pounds.

DR. MACK: 2,000,000 pounds of yellow metal or one and one-half million pounds of red metal was given as the life per lining. This is for the moving, indirect-arc type furnace. Converted, this would be about 1500 heats. Some linings will fail earlier than that, but 2000 heat lives are not unusual. Around 1500 heats mark the point, with present refractories, where replacement of the lining becomes advisable.

MR. CORNELL: Every steel plant engineer recognizes that there are first, second and third quality fire-clay brick. This is also recognized by the brick manufacturers. Why can we instead of having everything presented on first quality, not have something on second and third quality definitely stated?

MR. ROSS: No man likes to say first, second and third quality for his brick. The A. S. T. M. classifies one brick as suitable for a particular service and another brick suitable for some other service, etc. In a few years this should eliminate that trouble altogether.

MR. AYARS: In connection with Mr. Booze's paper[2] a statement was made that checker brick were commonly supposed to go at least to cone 31. I have seen some stiff-mud fire brick which I doubt would go above cone 27 or 28. These have been used with considerable success and a greatly reduced cost. In fact they gave much better results in the checkers than the first grade brick previously used.

It is a departure, I think from the usual practice. The men in charge of the plants said that their checkers cleaned up better; they had a larger percentage of brick that could be used over again when they put in their rebuilt checker work. That brick is made either in northern Kentucky or southern Ohio.

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[1] Discussion conducted at Atlantic City Mtg., Feb., 1924 (Refractories Division).

[2] "Checker Brick for Resisting Alkaline Slags," *Jour. Amer. Ceram. Soc.*, **7** [8], 594 (1924).

Mr. Howe: The life of fire-clay brick depends upon the design of the furnace. For instance, in the Illinois district they are using machine made checker, made from Cheltenham clay which seems to give very good results and on the other hand there are lots of open hearth furnaces where they have to use brick fusing as high as cone 32 or 33 if they can get them and yet they do not always get satisfactory results. They have to top them off with silica checker. This can usually be traced back to the furnace designs and relative proportions of the different parts.

While the subject of checker brick is being discussed, it just occurred to me that some work was done in England a year or so ago regarding the effectiveness of the different portions of brick. They seemed to think that even with silica brick the outer edge was the only one varying in temperature during the regular period of the firing. In other words, $2^1/_2$-inch checker would give all of the efficiency that was necessary because that would leave a $^1/_2$-inch center to give a certain amount of solidity to the structure. The conclusion reached in this paper was that it would be a fallacy to go below $2^1/_2$-inch checker and permissible to use only as thick a checker as would be consistent with solid construction.

Mr. Hewitt: We have seen at times where the furnace operator, in constructing his checkers, would use two different types of brick—a higher fusing brick at the top eight or ten courses and a lower fusing brick for the lower courses. We have also found at other plants that the practice is to use one grade throughout the checkers, the point being that from an operation standpoint there was too much danger of getting the brick mixed, when they are being laid. It will be interesting to learn whether or not the practice varies from district to district and which of the two is the more common method.

Mr. Dell: We have made checker brick with cone 28 refractoriness which gave good service over a number of years. Whenever they have had slag flashes or too much slag that was carried over, these bricks failed through this slag action.

What type of checker brick seems to give the best service; those ground fine and fired hard or those of a medium grind with a medium fire? It has been our experience that as long as the brick were well fired with a good medium firing, it did not make much difference whether they were very hard or not. In other words, the surfaces on hard fired and that of medium fired brick were about the same.

Mr. Spangler: I would like to discuss the use of silica brick with particular reference to the problems of the furnace roof.

One speaker mentioned that if the life of roof brick could be increased the open hearth furnace would be greatly benefitted. Before we get to the problem of increasing the roof life we need to consider the elimination of the minor repairs of the roof. These repairs during the course of a run, hamper the whole operation of the furnace. If the furnace is shut off every little while, for 20 minutes to an hour, for a roof patch, allowing the furnace to cool a bit, a fatigue strain is set up in the roof brick which probably increases the spalling rate and tends to reduce the total roof life.

If the refractory men could produce brick having a uniform life in all parts of the roof (and the rest of the furnace as well) throughout the life of the furnace, we then could consider lengthening the whole time of the furnace run by lengthening the life of the roof.

Minor repairs cost labor, material and furnace time. Of these three items, the greatest is furnace time, for an idle furnace means lost production. Mr. Cornell[1] gave a very complete discussion of furnace costs but apparently neglected to consider *lost furnace time*. Minor repairs, occurring in small driblets here and there, amount to a great deal of money in the yearly cost and constitute a considerable item in the cost per ton of steel produced. Refractory men can be of great help to the furnace operator by producing uniform quality of brick thus making possible fewer minor repairs.

Mr. Harrison[2] mentioned in his paper that lack of uniform physical structure of the brick has an effect on the need of roof repairs and on the final failure of the roof.

The fact that roof brick are not smooth and uniform in surface causes them, when placed in the roof, to crack. At the start of the furnace run the operator gets a nice glaze over his roof and in a few days (sometimes a week) a few ends of roof brick drop out. The glaze on that place is lost. The furnace is operating at its highest heat and that spot begins to weaken and burn and in a very short time minor repairs are necessary at that part of the roof. If the brick are a little warped they will likely be cracked when building the roof.

The masons have to build the roof as fast as possible to get the furnace back into production. They are not doing a fine piece of work such as is done on a fancy public building but are getting the roof in place as quickly as possible because an idle furnace means money lost. It means the biggest portion of the furnace cost. As a result the brick are put into place as hurriedly as possible. Warped surfaces are often placed next to each other instead of slowly fitting the concave and convex surfaces together. The load comes on the roof when the roof form is taken out and the lower part of warped brick is likely to crack. They may not drop out until the end or the first week but they will sooner or later cause weak spots which lead to roof troubles.

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[1] "Some Considerations Necessary in the Selection of Refractories for the Open Hearth," *Jour. Amer. Ceram. Soc.*, p. 670.

[2] "Roof Brick for the Open Hearth," *ibid.*, p. 698.

The manufacturers can increase the life of the open hearth furnace, not only in the roof, but in many other places by producing brick uniform in shape.

Mr. Cornell: Natural gas furnaces may lose 15 days production in the course of the year for rebuilding and producer gas furnaces may lose 20 days.

In the million-ton plant which I described, the loss of tonage due to open hearth not being a permanent structure is about 80,000 tons per year. That totals up to a big sum of money. One half of the lost time is caused by rebuilding and one half to operating delays.

Mr. Griffith: A silica brick wall fails first at or near the slag line or immediately above the basic material.

Frequently the top wall at a certain plant would be perfectly good while the center portion would be useless even for salvage. They put in lump chrome for backwall about 22 inches thick at the bottom and tapering back to about 8 inches. They very rarely replace the bottom. That backwall costs them a little over twice as much as an original new silica wall. It lasted them four times as long. The top wall was patched along the skew-back. I saw a front wall last week in that plant that just had the one hundred third heat. The wall was perfectly good. You could almost lay your hand on the bottom. There were a few little red spots along the skew-back. They would replace those little spots and thus get full life of furnace out of each wall.

One particular plant, visited recently, had one furnace on oil. They had trouble with their bulkheads. They seemed to melt them right down on the outgoing end. That, reversed, gave them the same trouble on both ends. Their oil pressure was about the same pressure as that of their air. In other words, to atomize their oil they were using air which should have been used only for combustion, and consequently were blowing their fire clear over to the bulkhead. They blamed that on the brick. That was the first impulse. The brick had nothing to do with it.

Mr. Howe: I wonder whether chrome brick would be satisfactory in the front wall of the Talbot furnace.

Mr. Griffith: That constitutes the roof when you are tapping. There is some possibility of using chrome brick in that type of furnace. They have tried magnesite brick. While we have improved considerably the physical strength of chrome brick, I doubt very much if it would give them any better service than they have had with magnesite. The spalling would be very much less but I do not believe their trouble is due either to spalling or fusion. I think that it is due primarily to the fact that that is a suspended roof with nothing to hold it but the brick at top and bottom. No brick will stand in there unless they tie it in some way or arch it as in a roof. You would not build a roof of an open hearth furnace upright, then turn it over and expect to have a perfectly flat roof which would stay there. That is literally what you do when you tilt a Talbot furnace. You have not provided for a roof. That is not the fault of the brick. It is the fault of the designer.

MEMBER: Is the failure of silica brick due to the structure of the brick or to the rapid heating up?

MR. SPANGLER: The too rapid heating up of a new roof will always cause failure. If we get a shorter roof life than our long series of records leads us to believe we should get, we then investigate the cause of the failure. The irregular brick structure of silica brick is the final cause of patching in a roof. The irregular structure is one of the causes of patching a roof, one of the things that makes necessary minor repairs. Ceramists and refractory engineers might make wonderful brick as far as non-spalling is concerned, but if the manufacturer turns out that same brick in warped and non-uniform shape, the furnace is not going to be much better off. That is what happens with a good many of our silica brick today. The brick are not regular in structure. In the arch they bear the load of the weight of the whole arch. Strains are set up when two concave surfaces of adjacent roof tiles are facing each other. Something has to give way. Those warped brick give way sooner than brick which have surfaces uniformly in contact with each other. I look upon that as a manufacturer's problem for which the open hearth operator pays.

MR. BOLE: Mr. Howe, do you consider that there is any chance for improving mechanically the shape of silica brick? Are there any possibilities in the mechanical molding which is now being developed?

MR. HOWE: Silica brick are being made now by machine. They were made a good many years ago by the die process but the results were not entirely satisfactory. It was tried in this country at the Niles plant and abroad in England. Die pressed silica brick were never popular but more recently they have developed a machine which more closely duplicates the hand process. The material, instead of being thrown in by the molder, is dropped. The force of the drop is equal to the force which the molder would give when throwing the material into the mold. In that way the mold is filled out properly. It gives some trouble in getting absolute uniformity in the amount of material that drops into the mold to fill out the shape, but under careful control it is possible to make a silica brick that may be used interchangeably with a hand-made silica brick. One company is now building a larger machine and three other companies are figuring on new installations. From that it seems that the advent of the machine-made silica brick is here.

MR. AYARS: Occasionally a piece of brick drops out. Is that more often caused by irregularity in the shape of the brick or is it because of a slight crack in the brick due to rough handling in transit or by the mason?

MR. SPANGLER: It is not caused by an original crack in the brick. The brick mason taps each brick with his hammer as he puts it in place. If he found a brick with a punky ring, indicating a crack or internal defect, he would discard that brick.

MR. AYARS: Do you exercise rigid inspection as to shape of your brick?

MR. SPANGLER: We do not, because there has been no acceptable specification for silica brick universally used. One thing I think the AMERICAN CERAMIC SOCIETY is going to do for the brick consumer is to put before the manufacturer and consumer specifications which we will agree are working specifications. These will be the basis of inspection.

When we receive a carload of brick which does not look good to us (and I say that advisedly because that is our main means of detecting poor brick), we test some of them chemically and physically. Then we have an argument with the brick company. We send them some and say that the brick ordered were first class brick. What constitutes first class brick? We have heard that discussed here in the meetings a good many times. Ultimately the consumer hopes that the problem of specification will be ironed out and that there will be a common measuring stick for everybody to go by in the acceptance and rejection of brick.

MR. AYARS: In the case of silica brick I believe that the consumer is absolutely justified in requiring a brick that we can put a straight edge on—across any corner or from side to side.

MR. SPANGLER: We are unable to get such brick from the manufacturers.

We would like to ask the manufacturer to give us a certain percentage of brick which would stand a straight edge diagonally—what that percentage should be we hope the Specifications Committee will sometime tell us. We could not ask the manufacturers to give us 100% straight. They would in turn ask us if we wanted the brick goldplated.

MR. AYARS: The average manufacturer of silica brick is trying to furnish a straight brick but there are many operating details in a silica brick plant that get away sometimes and crooked brick may result. Is there a hammer inspection of each brick as it is laid? Do you use a $13^1/_2$ inch roof?

MR. SPANGLER: $13^1/_2$- and 18-inch rings.

MR. AYARS: The average open hearth roof is laid under the direction of one good mason by labor that commonly shoves a pick.

MR. SPANGLER: Our roofs are laid by experienced brick masons.

MR. BELL: Premature failure of an open-hearth roof may at times be traced to the breaking or spalling of even a very small number of brick, or as it is sometimes called, unit failure. The end of a single brick becomes detached by spalling and falls out. A hole or pocket is thus formed in the roof and the adjoining brick are then the more readily attacked by the furnace gases.

One defect which has not been mentioned is that of sponginess or poorly filled out brick. Brick with spongy corners are naturally weak and hence more liable to spalling and failure under load. Brick to best withstand open hearth service should not only be true to shape but also of sufficient mechanical strength to support the structural loads imposed upon them.

MR. NESBITT: A large part of Mr. Spangler's troubles are due to poorly shaped brick. The mechanically made brick are true to shape. The hand-made brick are not always that way. Mechanical brick can be placed on one end 5 or 6 feet high without toppling them over. You cannot do that with hand-made brick.

In nearly all cases where the brick pinch off and start a place in the roof such as Mr. Spangler described, it is really chargeable to want of trueness in shape of the brick.

If a large particle of ganister gets into a brick it is needless to say that when it starts to heat, its expansion is not going to be the same as that of the brick. It pinches off a piece of the brick. There will be a weak place in the roof right away.

MR. AYARS: There are other things besides molding which enter into the shape of the brick. Chief among them is the shape of the pallets on which they are dried. If these are not perfectly smooth and true the brick will be warped. That will happen in a mechanically made brick although the edges appear to be true. The pulling of the end of the brick is hard to get away from in hand molding but I believe that a perfectly true brick as far as the two flat surfaces and edges are concerned, can be made by hand molding. It is the fault of the pallet or of the moving of a car from the molding table to the drier that dictates the shape, particularly with silica brick.

DR. MACK: It is not exactly clear to me why the spalling or dropping of a comparatively thin piece from the silica roof in the open-hearth should result in its complete failure. From Mr. Spangler's remarks, he considers this connected with the breaking of the continuity of the glazed surface previously produced when a new roof is put on and brought gradually up to operating temperature. A smooth glazed surface is evidently a desirable condition to have but just why the falling out of a small area, 3 inches thick, from a thirteen or eighteen inch roof should bring about failure is not quite clear to me. I wonder if I can get a little more enlightment. Is subsequent "burning-out" due to chemical erosion, mechanical abrasion, or some other action? I would like to get straightened out on the physical chemistry of the process by which the roof is brought to failure.

MR. SPANGLER: When a 3-inch piece of one tile drops out, leaving a break in the glazed surface of the roof, there is exposed to the flame at the highest temperature the bottom part of that raw tile as well as 3 inches of side surface of the surrounding brick. Those brick have no chance to glaze because they are not heated slowly. The furnace is operating at its fullest extent, therefore spalling takes place and actual burning of the brick represented by dripping. In a short time a hole appears in the roof at that place. That hole must be patched. The patch is fresh brick which have no chance to become glazed. The furnace has been shut off only 20 minutes while that patch is put in. In a few minutes it is back again operating under full heat. The new brick then begin to spall; they do not have a chance to glaze. That continues on in that one place, and many other places like that throughout the roof, until the roof finally fails.

DR. MACK: After spalling takes place you do not get re-established the glazed roof surface but you do get actual fusion and dripping from the unglazed area exposed. This would be convincing if it could be shown that the material at the uneven surface exposed by the spalling actually had a lower fusion point than that of the vitreous material making up the remainder of the roof surface.

MR. SPANGLER: I believe so but I cannot prove it.

MEMBER: If 3 inches of brick fall out the support of adjacent brick is gone. They also will break off and in no time there is quite a hole in the roof. It is generally accepted that every joint in a wall, especially walls of open hearth furnaces is a point of attack; that if we could have a wall of one piece with a perfectly smooth surface to start with and could keep it from cracking, that wall would last longer than a wall made of a number of units of the same material.

One of my open hearth friends performed a very interesting experiment which has a bearing on this. He built the two opposite ends (the bulkheads) out of brick. They were exactly the same excepting that for one end of the furnace he went to the expense of grinding the brick until they were brought to absolutely true surface, such as you might get with machine made die pressed brick. Those were laid in place without any mortar joints whatever. The bulkheads in the opposite end of the furnace were built up of ordinary brick as they came from the manufacturer, using the regular practice of laying up. They used these brick in opposite ends of the furnace in order that they would be subjected to exactly the same treatment and get a real comparative test. The net result was that the brick that had been ground to true surface lasted out five times the brick in the other end. The brick that were not ground to true surface had to be replaced five times before the others did. This, however, was in a small furnace.

MR. DORNBACH: From the standpoint of manufacturers, symposiums are very welcome. Next to seeing the special requirements, I know of nothing better than to listen to remarks passed out by the users of refractories. The manufacturer has a terrific amount to contend with because everybody in the manufacturing game knows that in different places you meet different conditions where you are supposed to find practically the same thing existing.

Mr. Cornell: Mr. Spangler brought out some very important things in the discussion of handmade and machine-made brick. The A. S. T. M. have gone into this quite thoroughly but I do not think the metallurgist is a ceramist. Mr. Spangler says we must get together, the ceramist and the steel man, and get a set of specifications that will suit everybody. How are we going to get that set of specifications? The A. S. T. M. may compile one but that does not mean that they will be accepted.

Mr. Spangler: I might say that we have paid very little attention to spalling tests in our own experimental work because we have felt that spalling is tied in with other tests which are more conclusive such as the chemical analysis, the apparent specific gravity and porosity. Those three items have a certain control over spalling and we admit, without being able to remedy it, that spalling occurs wherever expansion and contraction occur. The minimum amount of expansion and contraction will give the minimum amount of spalling. We know that to be a fact and have no way of getting around it. We have paid very little attention to spalling tests in our own work. We have just observed relative spalling of various kinds of brick and have tried to get those which showed the least amount of spalling.

Mr. Griffith: If a brickmaker has a brick that gives in the open hearth 318 heats where he has been getting an average of 215 heats, and pleased to get that, and he asks one dollar per thousand extra, you quit buying his brick. Where, then, is the incentive outside of the personal pride in making the brick to give you the service you think you ought to have?

Mr. Spangler: Mr. Griffith has mentioned a very vital point and one which I think the brick consumer will have to fully appreciate and realize if he is going to get proper coöperation from the manufacturer. We think, in our own plant that we have realized that because we are basing our requests for brick to the purchasing department on the results of our records of service life in cost per ton of steel rather than in dollars per thousand of brick delivered to the plant.

Mr. Ross: Glass manufacturers feel that frequently in the crowns of glass melting furnaces a good deal of the breaking of the brick in the heating of the crown is due to non-uniformity of the firing of the silica brick. Some of the brick have been fired hard and hence have a given expansion and some of the other brick in which the quartz has not been transferred to the other forms of silica will continue to take on further permanent expansion. Do you find that irregularities in the firing of silica brick bother you any?

Mr. Spangler: We have not observed that in roofs. But I believe such a condition would lead to trouble.

Mr. Matheson: Mr. Spangler has brought out many points that have given us all trouble. We have had our trouble with spalling. We call it gobbing. Mr. Spangler referred to it as brick defects. There is a whole lot in the way a roof is laid up. If the brick are not keyed up properly the tendency is for the roof to sag leaving the bottom part of the joints unprotected. The entire strain or weight of the roof is on the outer part of the brick and then the defects that Mr. Spangler refers to will occur. Any silica brick when brought up to heat is going to show defect on account of its high coefficient of expansion. On the other hand if the turnbuckle rods are tight, expansion will raise the roof, opening up a portion of the joints and throwing the entire weight of the roof upon the lower portion of the brick and then spalling will occur due to a shearing action which has been brought upon the brick. This may not be 100% our practice. It is my belief, however. I have tried it and it works all right.

The brick are laid in dry, driving in a tight key. We gage the most of our brick before we put them in. We submit them to a visual inspection. We always take some brick from the cars and send them to the laboratory for physical and chemical analysis. We instruct the men to be careful that that key fits both top and bottom. We try to get the key in so that it takes uniform bearing from the very top of the brick down to center before we take out the wooden centers. We have our men under the supervision of competent foremen.

Mr. Howe: Mr. Matheson, where a portion of the roof was raised more than another as cited by Mr. Ross are the strains or different pressures causing this due primarily to volume changes within the brick?

Mr. Matheson: I never noticed that to be the case where a section of the roof went up higher than another. If we find light colored brick in our roof we take them out. We do not as a rule put any light colored brick in the roof.

Mr. Ayars: Mr. Matheson spoke about gaging the brick. Do open hearth operators gage brick received or possibly just before putting them into the roof? Do they put a straight edge on them?

Mr. Matheson: We have a standard method of gage inspection. We allow a tolerance of under or over a certain per cent. That we are not as particular about as the uniformity in thickness. Sometimes we find a carload of brick that runs slightly over $2^1/_2$ inches in thickness. Others will run slightly under. When those brick are uniform throughout the entire carload, whatever the lot consists of, then, we consider them as satisfactory. We always gage our brick as to uniformity and as to straightness. We do not gage every brick in the car but we take them out here and there and at random and gage them. If we find too many in the car that are warped or do not show even corners, then we go through the car very thoroughly. If we find the first 8 or 10 brick are satisfactory we accept the car as being O. K. The same applies to uniformity and thickness. We allow a tolerance of $^1/_4$ inch per foot.

Mr. Ayars: Would you prefer them to be a little under thickness than over if you are going to have a variation?

Mr. Matheson: I have never paid attention to that.

The matter of glazing has also been discussed here. We experimented somewhat with that. It is not the temperature of the furnace that causes the glazing. The fine particles of the brick are worked to the surface, to what is known as the skin of the brick. The surface of the brick will vitrify where the porous interior of the brick will not. If a half brick is suspended in a furnace, the portion of the brick containing the original skin will glaze where the fractured surface of the brick will not.

Mr. Brooks: It would be interesting to know what service tests for refractories the open hearth men are using to determine proper applications of refractories to their needs. Certain practical operating tests were mentioned. What is the nature of such tests?

Mr. Spangler: We first make laboratory tests as is done in any laboratory and then we install the type of brick we are experimenting with in a section of the furnace right beside the type of brick which has been previously used and with which we are acquainted. Then we observe that test installation every day as long as it lasts and make complete notes on its history. At the end of its life we can compare it with our experience on the type of brick which we are using in that particular place.

Mr. Furness: There is no question but that an open-hearth operator will run his furnace to the maximum temperature that the brick used in the construction of the furnace will endure. That part of the furnace which is most vital, and the failure of which causes the longest repairs, and the most expensive repairs, even at times going into a general repair, is the roof. Therefore, since, in the course of the discussion it has been mentioned that certain standard silica brick will, on account of their perfection as to shape and manufacture, give greater endurance, the open-hearth man would like to have these produced as a special quality brick for roofs.

Further, if there is any method by which the ceramic engineers can increase the ability of these brick to resist high temperatures, this should be applied to the manufacture of these special brick. I feel, however, that there are many other problems of nearly equal importance to the brick used in the construction of an open-hearth furnace, on which much help could be given to the steel manufacturer by the American Ceramic

SOCIETY. For example, runner-brick, sleeves and nozzles—the latter in particular. The difficulty of obtaining a material which will resist the erosion of the steel at the high temperature at which it is poured is certainly great, and, at times, one is discouraged by the inability to obtain the material which in any way approaches that which one would desire. So far, I know of no nozzles, runner-brick, sleeves or ladle linings which are satisfactory.

All of these remarks apply to the manufacture of "quality" or high-grade steel. While important, they are not of such vital importance in the "tonnage" plant as in a plant which manufactures only "quality" or high-grade material.

I regret that the suggestions which I can offer to improve the conditions, are very few, but feel that, if any good ceramic engineer devoted a little time to the matter, he could improve all runner-brick tremendously. It must not, however, be lost sight of that these brick must be produced at a minimum cost.

I do not, at present, know of any clays, or clay-brick, which are used in ladle linings which are not strongly acid, yet one expects these to resist hot basic slags.

Considering nozzles, the importance of this piece is evident, particularly where it is necessary as in "quality" material to have a good control of the stream. Yet, but little attention is paid to the material, and still less to the waring and increase in size of opening.

I would suggest a brick for ladle lining which has a neutral or basic reaction when hot; for nozzles the material should be one that would resist the erosion of hot steel.

DISCUSSION ON THE DISINTEGRATION OF CLAY REFRACTORIES IN IRON BLAST FURNACES

BY S. M. PHELPS

The disintegration of iron blast furnace linings has been studied by Nesbitt and Bell.[1] They found that, under certain conditions, iron oxide in clay refractories acts as a catalyzer, by converting the carbon monoxide of the furnace gases into carbon dioxide and free carbon. The carbon is liberated where catalysis occurs, thus forming a deposit about the nucleus of the iron compound. This deposit of carbon gradually grows and in time acquires sufficient size to disrupt the structure of the brick. The deposits in the brick vary in size from those hardly visible to half an inch or more in diameter. The carbon is usually of a soft soot-like nature, but at times assumes a graphitic character.

In practice, the degree of disintegration varies from small cracks to complete disruption, forming a dark gray sand-like material. It occurs in zones about parallel to the inner surface of the lining and varies in thickness from a few inches to a foot or more. In areas of disintegration, a perfectly sound brick is often found, which at the present time has not been satisfactorily explained.

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[1] *Iron Trade Rev.*, 1603–1607 (1923).

Disintegration is often a contributing cause for "blowing out" a furnace, but rarely a direct one. It seems to be more prevalent today than 15 to 20 years ago.

The results of the experimental work on this subject by Nesbitt and Bell may be summarized as follows:

1. The iron oxide must be in an uncombined state to be catalytic.

2. Catalysis begins at 300°C and continues until 525°C, being most active at between 420 and 470°C.

3. The higher the concentration of the carbon monoxide in the gases, the more pronounced the action.

4. The higher the percentage of free iron oxide, the greater the disintegration.

Nesbitt and Bell found that brick made by the auger machine fracture along the lamination lines, steam-pressed brick split lengthwise, while hand-made brick fracture very irregularly.

Suggested Preventive Measures

Inasmuch as the gases of the blast furnace cannot be changed, the remedy must be in the refractories.

The ideal brick would be made of clays free from uncombined iron oxide. As an alternative, the ordinary clays could be treated to remove the objectionable iron compounds by weathering or otherwise.

Hard-burning affects the solution of iron compounds, thus destroying their catalytic property, but may make the refractories too sensitive to thermal shock.

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ORIGINAL PAPERS

SUGGESTIONS FOR DEVELOPMENT IN ENAMELING TECHNOLOGY[1]

By Homer F. Staley[2]

ABSTRACT

This paper comprises the address of the Chairman of the Enamel Division of the American Ceramic Society at the Atlantic City Meeting, February, 1924. Among the suggestions for development in enameling technology are: The more general use of melted weights in representing enamel compositions; the use of coefficient of thermal expansion factors; improvement in the mechanical properties of enamel glasses by increasing the percentages of zinc oxide, boric oxide and titanium oxide, and by the use of thinner coatings; the widening of the heat range of ground coat enamel compositions by the use of more complex compositions than are now employed; and, finally, the more careful control of variation in the composition of the feldspars used in making enamels.

Introduction

It should be understood that in choosing the above title, the writer fully understands that enameling technology in this country has been making rapid advances during the last ten or fifteen years, and has already reached a high state of development. In fact, the enameled wares made in the United States surpass both in quality and quantity those of any other nation. Notwithstanding the present enviable position of the industry, it certainly will not be out of place to consider the lines along which it seems possible to make even greater improvement in the future.

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[1] Received April 7, 1924.

[2] Chairman's Address (Enamel Division), Atlantic City Meeting, Feb., 1924.

Probably because the American nation as a whole has a peculiar genius in the application of mechanical ingenuity to manufacture, and for the development of systems of mass production of wares with high priced labor at comparatively small cost per unit of ware produced, advances in ceramic technology and suggestions for future development have been more prolific in the past few years in the branches of technology dealing with the equipment and methods used in the preparation of shapes, the melting and grinding of enamels, the application of enamels, and finally the firing of the wares. Very rapid progress along these lines seems assured. Therefore, these remarks will be confined to the rather fundamental question of enamel mixtures and possible improvement in these.

Use of Melted Weights

Possibly, one of the greatest advances that could be made would be the more general use of the system of representing enamel formulas in calculated percentage amounts of melted materials. In this system, the relations of the various ingredients in the enamel are not obscured by the presence of variable amounts of volatile ingredients and by the fact that the same oxide is often introduced by several chemicals. It makes it possible to calculate the percentage of each oxide present in the finished enamel and to determine at a glance whether the total for any oxide exceeds the allowable limit.

An outstanding advantage of this method is that it enables the enamel maker to apply to his mixtures the data available in the literature in regard to the effect of variation in chemical composition on variation of the mechanical properties of enamels and glasses. All such data are given in terms of the percentage composition of the melted enamels. The use of such factors has its scientific basis in the fact that enamel glasses are really solutions and therefore their properties are additive functions of the properties contributed by the constituent oxides and radicals. The most hopeful line for rapid development in the enameling industry lies in the use of data now available and in the securing of more data in regard to the effect of variation in composition on such properties of enamels as the coefficient of expansion, the tensile strength, the elasticity, the ability to stand impact and the acid resistance.

Factors for Coefficient of Thermal Expansion

The most commonly used of the factors available are those for coefficient of expansion determined by Winkelman and Schott[1] for glasses and by Mayer and Havas[2] for enamels containing opacifiers. I am well aware that in publications coming from the Expansivity Section of the Bureau of Standards the statement has been made twice[1] that the use of these coefficients is not accurate. The study of the data presented in these publications in regard to the difference between the actually determined expansivity of enamels and that calculated by the use of these factors, indicates that while the factors possibly are not accurate from the standpoint of a highly specialized physical laboratory, they are sufficiently accurate to act as a very valuable guide in the technical control of enamel mixtures. They are certainly much better than no factors at all. The Bureau of Standards can do a valuable service for the enameling industries of this country if it will add to the list of factors now available and will furnish more accurate factors for use in cases where they consider the present ones unsatisfactory. In the meantime, quite a number of enamel makers have been using the present factors with great advantage.

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[1] "Jena Glass" by Hovestadt, p. 217.

[2] *Sprechsaal,* **42,** 497; **44,** 188, 207, 220.

At this point it seems appropriate for the writer to say that in his Technologic Paper No. 142 of the Bureau of Standards, he was not enthusiastic about the use of these coefficients. Since that paper was written he has used certain of them extensively with uniform success and has come to have considerable confidence in them.

The coefficients of cubical expansion of the various kinds of enamels used in sheet steel vary from 0.0000280 to 0.0000330. Inasmuch as the coefficient of expansion for steel is about 0.0000412, the typical enamel must be under considerable compression. Elementary principles of mechanics show us that an enamel which is under compression will be much more liable to fishscale, and also to be damaged by impact in use, than one which is not under compression. Therefore, it seems logical to assume that steel enamels in general would be improved if they had higher coefficients of expansion.

The tendency noted in the past few years to use compositions in which all the quartz is replaced by feldspar is in line with this suggestion. The main advantage of using feldspar is that in this way alumina is increased which raises the coefficient of expansion. The use of cryolite in ground coat enamels is a very easy way to get a high coefficient of expansion in these, but unfortunately cryolite shares with fluorspar the property of giving vesicular structure in ground coats. Therefore, its use is not entirely satisfactory. In enamels for wares not to be used for cooking purposes, lead oxide may be used to give higher coefficients.

The replacement of about $2^1/_2\%$ of silica by high grade rutile in the case of ground coats and colored enamels and by iron free titanium oxide in the case of white enamels furnishes a means for raising the coefficient some ten points and at the same time obtaining the advantages of longer heat range, improved mechanical strength and marked increase in acid resistance. More than 3% seldom goes into solution but remains in suspension in the enamel and increases the opacity.

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[1] *Jour. Amer. Ceram. Soc.*, **4** [8], 620 (1921); **6** [10], 1011(1923).

In regard to the use in general of substances sparingly soluble in enamel glasses a distinction must be made in the effect of the part that goes into solution and the part that remains in suspension as solid material. Thus titanium oxide in solution has a cubical coefficient value of 4.1 and raises the coefficient of enamels, while titanium oxide in suspension has a coefficient value close to that of other solid opacifiers, around 2, and lowers the coefficient of most enamels. On the other hand zirconium oxide in solution has a low coefficient value very close to that of silica in solution (0.8), while in suspension as an opacifier its coefficient value is 2.1.

Increased Mechanical Strength of Enamel Glasses

Many years ago Winkelman and Schott[1] pointed out that the strength and elasticity of glasses were important factors in their ability to stand sudden heating and cooling. They introduced the term "thermal endurance" to denote the power of a glass to withstand thermal shock and deduced the following formula:

$$F = \frac{T}{Ea}\sqrt{\frac{K}{Dc}}$$

where T is the tensile strength; E, Young's modulus of elasticity; a the linear coefficient of thermal expansion; K the conductivity for heat; D the density; and c the specific heat. The properties directly affecting the thermal endurance are tensile strength, elasticity, and coefficient of expansion, the remaining factors being proportional directly or inversely to their square roots.

Since enamel glasses are attached to metal, the difference between the coefficient of expansion of the enamel and the metal base must be considered and the formula showing the more important factors for thermal endurance of enamels may be written:

$$F = \frac{T}{E(a-a')}$$

in which a' is the linear coefficient of thermal expansion of the metal, and the other letters have the same significance as above. Aside from the difference in expansion coefficients the ability of enamels to stand strain is expressed by the relation $\frac{T}{E}$. In Technologic Paper 142, of the Bureau of Standards, page 119, the writer has used the last expression to derive factors indicating ability to stretch given to glasses by various oxides.

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[1] "Jena Glass" by Hovestadt.

The relative order is as follows:

Zinc Oxide	100.0	Barium Oxide	5.0
Boric	32.5	Alumina	3.1
Silica	13.8	Sodium Oxide	2.0
Lead Oxide	5.3	Potassium Oxide	1.7

While the values given are open to some question on account of the small number of glasses studied, the order of the oxides in this set of factors agrees qualitatively with practical experience in enameling. In enamels of given fusibility, those high in zinc oxide, boric oxide and lead oxide give less trouble from crazing and chipping than those high in alkalies. Barium oxide occupies an intermediate position, according to the experience of the writer, as it does in this list.

Little is known of the effect of other enamel making ingredients on the mechanical properties of enamel glasses. It is generally accepted that calcium oxide, fluorspar and cryolite have an unfavorable influence. The effects of zirconia have been studied by Wenning[1] and by Wolfram.[2] In general the effects seem to be favorable. Titanium oxide also has a very decided effect in increasing the mechanical strength of enamel glasses. W. E. S. Turner[3] points out that titanium raises the thermal endurance of glasses in spite of the fact that it raises the coefficient of expansion, which is detrimental in glasses. On the other hand, the increase of coefficient of expansion is an advantage in enamels, and we get the full advantage of increase in mechanical strength imparted by titanium oxide.

Increased strength and elasticity of white enamels could be obtained by the use of much more opaque enamels than are at present employed and their application in much thinner coats. This would mean that instead of using 4 to 10% of opacifiers on the mills, that from 10 to even 20% would be used as is the custom in foreign countries. It would also mean that instead of grinding the enamel to a comparatively coarse consistency, it would be ground quite fine. Contrary to accepted belief, the use of such large amounts of opacifiers would be economical since the weight of enamel used would be so much less. According to the principles of mechanics and also according to common experience, the mechanical qualities of enamel coating, such as elasticity, resistance to impact and adherence to the steel, are tremendously improved by the use of thinner coatings.

Widening of Heat Range

Quite a number of the types of compositions used for enamels which are applied in thin coatings, such as ground coat enamels for sheet metal and cast iron, and one-coat gray enamels for steel, have comparatively short heat ranges. That is, there is only a narrow temperature range between the point at which the enamel coating becomes sufficiently fluid to adhere to the metal and the point at which it burns off at spots on which it is particularly thin or which become particularly hot. The workability of these compositions would be greatly improved if their heat range could be widened.

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[1] *Bull. Amer. Ceram. Soc.*, **2** [5], 102–4(1923).

[2] *Jour. Amer. Ceram. Soc.*, **7** [1], 1–13(1924).

[3] *Pottery Gaz.*, **48,** 607–17.

The temperature at which enamels have sufficient fluidity can be lowered only by adding materials which will make the compositions more fluid at low temperatures. The drawback to doing this is that in general, but not in all cases, such additions will also lower the temperature at which the enamel burns off.

The temperature at which the enamel burns off or volatilizes on heating can be raised by making the composition of the melted enamel more complex. Without dwelling on the physical chemical relations underlying this effect, we may say that melted enamels are essentially like salt solutions, and the greater number of compounds in solution one in another in the enamel, the higher the boiling point or volatilization temperature of the enamel. Without knowing the compounds actually formed in melted enamels, we can safely assume that by adding a new element which goes into solution in the enamel mixture, we are making the composition of the melted enamel more complex and will give it a higher volatilization temperature. By careful selection of elements for addition, we can also make the enamel more fluid at low temperatures, and thus widen the temperature range both at the bottom and at the top.

Among materials not at present in general use in ground coat enamel glasses which may be introduced with advantage are lead oxide, zinc oxide, zirconium oxide and titanium oxide. With the exception of lead oxide, these materials may also be used in one-coat gray ware enamel glasses. For these uses it is satisfactory to use natural zirconia minerals as a source of zirconia and rutile as a source of titanium oxide.

One principle that seems to be fundamental in making a good ground coat for cast iron is that when the ware goes into the furnace, the ground coat should contain a certain amount of raw material. The presence of this can be secured either by melting the frit only to a thick paste in which case part of the sand used in all such frits is only partially dissolved, a certain part remaining undissolved, or by adding raw material at the mill. The philosophy of the presence of this raw material seems to be that as the ware heats up the raw material is gradually dissolved by the rest of the glass and the glass does not volatilize so readily. In general, we may say that the amount of this raw material should be not less than 15% of the melted weight of the glass and not over 35%. Attempts have been made to use larger amounts of raw material than 35%, but in such cases it is not absorbed into the rest of the enamel coating, but simply remains on the casting as inert material, while the rest of the glass is burned to a cinder.

Control of Variation in Feldspars

Probably the greatest avoidable loss in enameling of metals is that due to variation in composition of feldspar. As is well known commercial feldspars are not definite minerals but mixtures of two or more varieties of feldspar with other minerals, the chief of which is quartz. Therefore, various shipments of feldspar, even those from the same mine, will vary in composition. The most harmful effect of this variation is the variation it produces in the coefficient of contraction of enamels. The fact is that variation in feldspar has and is still causing more trouble in enameling of metals than any other one thing.

There are only two real solutions to the problem. The first is to use no feldspar and to make silica the chief refractory of the enamel. The second is to obtain an accurate analysis of each shipment of feldspar and to adjust the enamel mixture to the variation in composition of the feldspar.

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SILLIMANITE[1] DEVELOPMENT IN SOME TYPICAL CLAYS[2]

By Hobart M. Kraner

ABSTRACT

The question of sillimanite development in clays during firing is given theoretical consideration. References are cited which indicate a change in the structure of the clay molecule immediately after dehydration. Since most materials in the amorphous condition have lower indices of refraction than crystals or crystalline aggregates of the same chemical composition, the development of sillimanite is traced by increase of the mean indices of refraction of the fired clay aggregates.

Results based upon this method show a rapid development of sillimanite between 900 and 1100°C.

Introduction

The development of sillimanite in porcelain where fluxes, fluidity, catalysis, and slow cooling play their parts has been considered by others. The same question has also been considered from time to time as it is related to better clay refractories. In most cases where microscopic evidence was depended upon as a criterion of sillimanite development, this evidence was based upon the appearance of a crystal large enough to be seen microscopically.

In the light of this present study, the theory advanced by Watts[3] to account for the failure of refractories under load at about 1350°C might be more plausible than was thought at that time. He suggested that the molecular rearrangement of the clay molecule incident upon the development of sillimanite causes a weakened structure, and consequently a failure if the refractory be under pressure. To refute or corroborate this statement it is necessary to show how sillimanite develops during the heating-up period, and how this development is influenced by the presence of native fluxes and the resultant liquid phases which develop with continued increase in temperature. Other workers have shown us little regarding the molecular constitution of the mass immediately after dehydration of the clay molecule or what takes place with additional heating until the appearance of the crystal sillimanite. Recent work[4] on the rational analysis of clays points out that there is a distinct decrease in its solubility in hydrochloric acid after a clay has been calcined above 700°C. It has been noted that the best temperature to which to calcine a clay in preparation for rational analysis is in the neighborhood of 500°C. This indicates a period of weakness of the clay molecule with subsequent molecular rearrangement which decreases the solubility.

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[1] An appendix giving the interpretation of the results here found in the light of the discovery of Bowen and Greig, *Jour. Amer. Ceram. Soc.*, **7** [4], 238(1924) follows this paper.

[2] Presented at the Atlantic City Meeting, Feb., 1924 (White Wares Division).

[3] *Jour. Amer. Ceram. Soc.*, **3** [6], 448–459(1920).

[4] K. Fuha (*Jap. Cer. Assn.*, **351,** 566(1921)).

R. Rieke, "Rational Analysis as an Aid to Technical Control," *Ber. D. Ker. Gesellschaft,* **3,** 24(1922).

Whenever a clay mass has been given sufficient fluidity by subjection to a very high temperature, sillimanite shows a readiness to crystallize even from fairly siliceous viscous melts cooled rapidly. The writer found that in some siliceous clays melted in the flame of an oxy-gas torch, it was almost impossible to obtain a glass free from sillimanite crystals which would form in the glass during the short period of quenching. With this indication of a marked stability of the sillimanite molecule, it is quite likely that after heating through the dehydration period the molecules are not unassociated. Between this dehydration period and the temperature at which the eutectic between sillimanite and silica, or some other complex eutectic of an impure clay is formed, it would seem that the heat treatment given the mass would assist this association of the stable phases, which in this case would be sillimanite and the stable phases of silica at the corresponding temperatures. After the temperature of the liquid phase has been reached, we would of course expect the solution of these solid phases, that one which is present in excess dissolving last.

Referring again to the marked tendency of sillimanite to crystallize from a melt, we can expect it to be a product of recrystallization in quite viscous masses and this recrystallization will cloud results in which the appearance of the crystal is taken as a criterion of sillimanite development during the heating-up period. Its appearance as a criterion of development is uncertain for the reason also that we are limited by magnification in the size of crystal which can be seen microscopically. The term "amorphous" has been used in cases where "submicroscopic" might better have been used. Because we cannot see crystals of sillimanite in the mass is not sufficient cause to state that submicroscopic or colloidal crystalline sillimanite is not present. X-ray analysis has shown[1] that there is a change in crystal structure incident upon and subsequent to the dehydration of the clay.

In the search for a microscopic method by which this progressive sillimanite development can be studied, the following are to be considered.

(1) Upon heating, kaolinite ($Al_2O_3.2SiO_2.2H_2O$) loses water, leaving Al_2O_3 and $2SiO_2$ which might be associated as Al_2SiO_5 and SiO_2, both probably amorphous and existing as individual molecules which have not yet arranged themselves into geometric units characteristic of their crystal habit. The latter development will probably take place with increase of time and temperature.

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[1] *Trans. Ceram. Soc.* (Eng.), **22,** 105–10(1922–23). Kaolinite dried at 110°C was shown to be crystalline by its X-ray spectra. After calcining to 700°C it showed only traces of crystal structure, and such particles were present in extremely minute or colloidal sizes. After calcining at 900° or 1000°, a well marked crystalline structure was found and was the same for several specimens, and were different from those obtained for kaolinite before firing.

(2) Crystallization in an amorphous mass as in (1) produces a change in mean index of refraction of the mass, and to the extent to which crystallization takes place. The effect of crystallization from such an amorphous mass is to raise the mean index of refraction of the mass. If dissociation takes place in the clay molecule with amorphous Al_2SiO_5 and silica as the products, the resulting index of refraction will be intermediate between that of a glass of sillimanite composition and of silica glass.

(3) If an aggregate of sillimanite and cristobalite in the anhydrous kaolinite ratio is heated, the index of refraction of the aggregate will decrease progressively as the melting proceeds, and will continue to decrease until the last of the crystal phase has gone into solution.

(4) If any mixture of amorphous Al_2SiO_5 and SiO_2 is melted, there is no change in state, and the mean index of refraction should not vary from that of the original aggregate.

Method of Investigation

b and *c* of Fig. 1 show the indices of refraction of glasses which are of interest in this study. They represent all compositions between pure alumina and pure silica and of course include most types of clays free of impurities, the amorphous phases of which need consideration. These glasses were produced by molding together with dextrine, mixtures of corundum and flint and melting them in the flame of an oxy-gas torch, either pulling the glass out into threads, or causing the molten drop of liquid to drop into a beaker of water placed within one or two inches of the flame. This latter method was found necessary to prevent crystallization in some of the

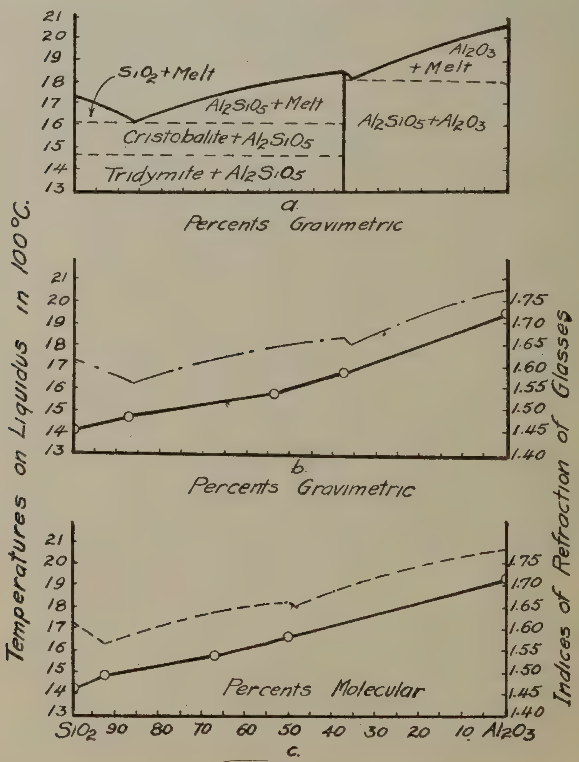

Fig. 1.

mixtures, but in the case of the eutectic composition and silica itself it was not necessary. The viscosity of each was so great at the melting points that beads could not be blown from the melting piece with the torch. Neither did crystallization take place readily in them.

In the case of anhydrous kaolinite composition, it was very difficult to obtain a glass free from sillimanite unless it was cooled by the above method. It is obvious that with this composition it is necessary for the glass to be free from sillimanite crystallization in order that the composition and index of refraction of the resulting glass shall be truly representative.

In the case of a chemical compound stable at its melting point, the melting is congruent. The liquid in equilibrium with the solid has the same chemical composition as that of the solid. It is therefore unimportant whether the measurement of the index of refraction of a glass of the composition of a chemical compound stable at its melting point is made in the presence of the crystal or not.

Indices of refraction of the minerals which might be of interest here are as follows:

Mineral		Index of refraction[1]		
Quartz		1.544		1.553
Tridymite		1.469	1.47	1.473
Cristobalite		1.484		1.487
SiO_2 glass	1.45			
Kaolinite		1.561	1.565	1.567
$Al_2O_32SiO_2$ glass	1.53			
Sillimanite		1.659	1.660	1.680
Al_2SiO_5 glass	1.58			
Corundum		1.760		1.768
Al_2O_3 glass	1.72			

It will be noted that the indices of refraction of glasses of the composition of anhydrous kaolinite or of sillimanite, vary considerably from the indices of the minerals themselves. It will also be noted that there is little difference between indices of refraction of silica glass, tridymite and cristobalite. If there is a change in the silica phases, the change of the mean index of refraction of the aggregate will be small, due to this small difference in the indices of refraction of the phases, quartz excepted.

For the purpose of studying the foregoing, the following five clays were chosen:

1. Tennessee Ball Clay, McKenzie, Tennessee.
2. Flint Fire Clay, Scioto County, Ohio.
3. Plastic Fire Clay (Tionesta) Shawnee, Perry County, Ohio.
4. North Carolina Kaolin, Spruce Pine, North Carolina.
5. Pure Crystalline Kaolinite, Red Mountain, Colorado (From U. S. National Museum).

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[1] U. S. G. S., *Bulletin* 679, "The Determination of Non-opaque Minerals"—Larsen.

Their analyses are as follows:

	1	2	3	4
Ign. Loss	8.53	12.90	7.87	16.83
SiO_2	61.23	45.20	57.35	44.50
Al_2O_3	25.05	36.77	27.96	37.55
Fe_2O_3	1.30	1.30	0.83	0.54
CaO	0.10	0.50	0.13	Trace
MgO	0.20	0.08	0.12	Trace
TiO_2	1.35	1.80	1.86	0.03
K_2O		0.52	1.32	0.75
	1.90			
Na_2O		0.00	0.21	
MnO			0.01	
$\frac{SiO_2}{Al_2O_3}$	4.15	2.09	3.49	2.01 molecular ratio

Half-gram samples of each of these five specimens were placed in small platinum envelopes and these charges, suspended from the bead of a platinum platinum-rhodium thermocouple, were then heated in a platinum resistance furnace for twenty-four hours at the temperatures desired. At the end of this time they were removed and cooled as rapidly as possible in the air. A small amount of each of these was ground in an agate mortar for a sufficient length of time to make them homogeneous and to cause any small particles of crystalline material to disappear by reason of be-

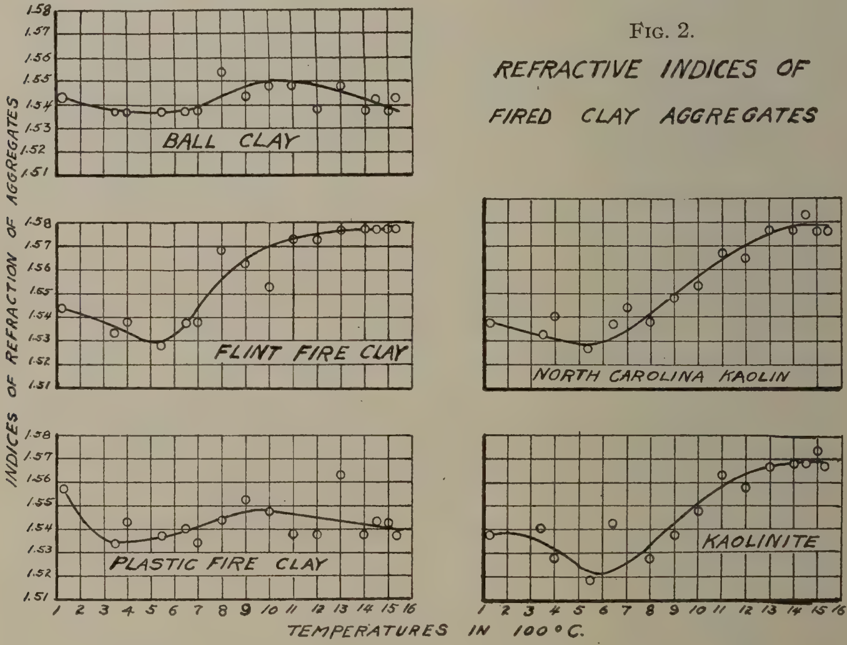

FIG. 2.

REFRACTIVE INDICES OF FIRED CLAY AGGREGATES coming an invisibly small particle in the aggregate. This usually required about thirty minutes grinding for each fired clay. The indices of refraction of the aggregate were determined by the immersion method, the Becke reaction, and in ordinary light. Values found are given in Fig. 2.

In order to study the completeness of the development of sillimanite at the higher temperatures, a charge of the pure kaolinite was melted completely and allowed to cool slowly over a two-hour period. This melt was pulverized as was done with other samples and the index of refraction of the aggregate obtained. It was found to be 1.578, this being only slightly higher than the highest indices of aggregate of the same clay.

Examination of the more coarsely ground aggregates shows the following:

Clay No. 1
Ball Clay

The impurities are largely quartz and micas. These are not affected by the heating until 1000°C is reached when the mica loses its optical properties, apparently disappearing by solution at about 1100°C. At 1200°C the whole aggregate assumes a mass birefringence which, under high power magnification, is plainly an intergrown and abundant sillimanite development. At 1300°C this is more plainly developed and at 1500° there is definite segregation of larger crystals and glass.

Clay No. 2
Flint Fire Clay

Quartz is the chief impurity and it appears principally in fine grained aggregates, which are present up to 1100°C. Some questionable traces of sillimanite are present at this temperature. At 1200°C the aggregates of quartz disappear into the mass which has assumed the mass birefringence, and at 1300°C distinct development of sillimanite is apparent.

Clay No. 3.
Plastic Fire Clay
(Stoneware Clay)

This is very impure, the micas being the chief impurities. Quartz and iron stain are present in large amounts. Mass birefringence is noted at 1000°C, while at 1100°C crystals of sillimanite are definite. At 1200° it is very well developed with the larger quartz grains still present. At 1300° the quartz persists, but slowly disappears with further increase of temperature. The sillimanite continues to develop into larger grains.

Clay No. 4. North
Carolina Kaolin

Muscovite mica is the chief impurity. A small amount of quartz is present. At 1100° some mass birefringence is apparent and at 1200° this is very distinct, showing considerable sillimanite, while at 1300° this is well developed.

Clay No. 5
Kaolinite

The crystals gradually lose their optical properties and pass to a nearly isotropic mass at about 600°C. They then begin to show mass birefringence which develops further at higher temperatures. Where the isotropic condition is complete, and where the mass birefringence begins to take form is hard to determine. The appearance of sillimanite is not definite until about 1300°C. At this temperature a lattice work of needles is formed which explains the change of the sign of elongation in the skeleton of the kaolinite crystal. The former crystal when lying on its basal pinacoid face gave a negative sign of elongation. The new crystal formation in it gives the old skeleton a positive elongation. The sillimanite crystals intersect so that the resulting angles are 65 and 115°. The line bisecting the acute angle is parallel with the elongated sides of the old crystal. Inasmuch as the new needles have positive elongation, the net result is a positive elongation for the new structure.

Interpretation of Results

From the results of Fig. 2 it would seem that:

1. Decrease of indices of refraction represent the passage into the amorphous condition.

2. The rapid increase of indices of refraction of the aggregate between 600 and 1000 or 1100°C is probably caused by the development of submicroscopic sillimanite.

3. The decrease of the index of refraction above 1200°C of the aggregates of the clays No. 1 and No. 3 which are high in silica and fluxes is probably due to the re-solution of sillimanite formed, or to the passing into solution of the silica minerals (usually quartz) which had not already done so; the effect of quartz being appreciable.

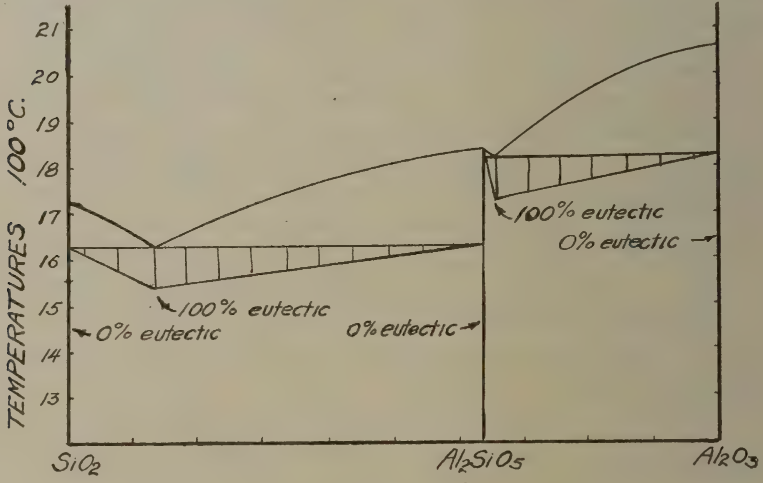

FIG. 3.

4. Applying No. 3 to the conditions which prevail at high temperatures, the generally conceded statement that "the bond gives way" in refractories is undoubtedly true.

In most cases the bond clay is of inferior refractoriness. The development of the sillimanite is indirectly the cause of the weakening of the refractory. Its development causes a segregation of the silica of the former clay molecule into the more impure portion, with a resulting increase of fluidity. Even in the very purest clay (see Fig. 3) a considerable quantity of liquid is present as soon as 1610° is reached. With increase of temperature the amount of liquid present increases. By intimate mixing and fine grinding with some form of alumina, the amount of silica sloughed off during the formation of sillimanite can be absorbed and thus more sillimanite formed and the amount of fluid decreased as the composition approaches that of sillimanite.

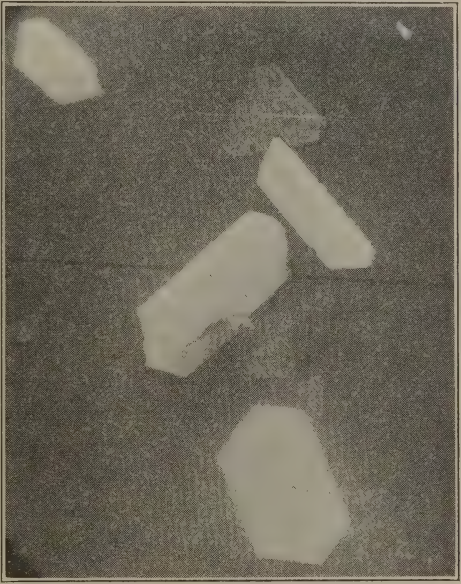

Fig. 4.—Clay No. 5 kaolinite between crossed nicols.

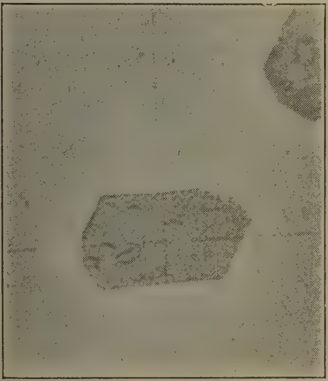

Fig. 5.—Clay No. 5 heated to 1350°C 24 hrs. Plane polarized light. Shows herringbone structure due to the development of sillimanite.

Conclusions

1. Sillimanite development seems to be a gradual rather than a sudden one. With progressive heating it probably begins as soon as the clay molecule is dehydrated.

2. The weakness of clay refractories at high temperatures is probably not due so much to volume changes incident upon the molecular rearrangement of the clay as it is upon attendant fluidity. The segregation of a very stable, refractory, fairly insoluble compound from the composition of the clay used, means also the segregation of the fluxes into the higher silica portion with a consequent increased degree of fluidity. The separation of sillimanite and the growth of the crystal might, therefore, be the indirect cause of this weakness.

3. Sillimanite development apparently takes place as abundantly in

clays which do not contain impurities as in those in which early fluidity operates to promote the size of the crystals.

4. When the mineral sillimanite develops from a kaolinite crystal, the direction of elongation of the new mass assumes the same direction of elongation of the former kaolinite crystal. In kaolinite the sign of elongation was negative whereas the new mass has a positive elongation.

Appendix

Inasmuch as the work given in this paper was completed before the presentation of Bowen and Greig's discovery that $3Al_2O_32SiO_2$ rather than $Al_2O_3SiO_2$ is the only binary compound occurring in the Al_2O_3–SiO_2 system, the interpretations and conclusions were drawn assuming sillimanite to be the compound which develops in clays upon firing. From the optical data presented, it may be readily seen that the discovery will not affect the value of previous petrographic interpretations on fired ceramic bodies in which this crystal was called sillimanite, and neither will it affect conclusions here drawn. Sillimanite has indices of refraction 1.659 and 1.680, whereas $3Al_2O_32SiO_2$ has indices of refraction 1.642 and 1.654. These indices still are considerably higher than the glass of this or any other composition in the system richer in silica from which this compound would crystallize. Such crystallization would raise the index of refraction of the aggregate, just as would crystallization of sillimanite from it if the latter were the stable phase. Therefore interpretations based on this method apply to the development of $3Al_2O_32SiO_2$ as well.

If $3Al_2O_32SiO_2$ separates from the composition $Al_2O_32SiO_2$ either by crystallization from the melt or by segregation during progressive heating, the material in excess of the crystal is richer in silica than would be the case if sillimanite were crystallizing. A greater amount of fluid portion is therefore present as soon as 1545°C, the eutectic temperature, is reached. This temperature of fluidity is easily lowered in clays by increased numbers and percentage of impurities.

Since neither sillimanite nor $3Al_2O_32SiO_2$ is stable at its melting point, glasses of alumina and silica containing them do not have their respective chemical compositions. Indices of refraction measured on these glasses would therefore not be representative of glasses from which crystallization had not taken place. The value for the index of refraction of glass of sillimanite composition given in the text is for a crystal-free glass.

Note: The author wishes to express his indebtedness to W. J. McCaughey and A. S. Watts whose advice and assistance made this work possible.

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THE DEHYDRATION TEMPERATURE OF PYROPHYLLITE AND SERICITE[1]

By J. L. Stuckey

ABSTRACT

Pyrophyllite and sericite are sometimes closely associated in works and the clays derived from them. They contain similar amounts of chemically combined water, but the sericite gives up its water more readily than the pyrophyllite, and is completely dehydrated at a lower temperature.

The dehydration temperatures of the hydrous silicates are of interest in connection with the changes that take place in the firing of clays, and since these materials are usually of variable and complex composition mineralogically, it follows that different clays may show a variable dehydration curve, depending on the nature and amount of hydrous mineral compounds present.

Among the minerals not uncommonly found in many clays is sericite, the finely divided form of muscovite. A mineral which may closely resemble it optically, and is sometimes found associated with it in some rocks, and residual clays derived from it is pyrophyllite ($H_2Al_2Si_4O_{12}$). This material, which resembles talc in appearance is also claimed by the producers to have been used in pottery manufacture; but the writer has not been able to confirm this statement.

During a recent investigation by the writer of the pyrophyllite deposits of the Deep River Region in Moore and Chatham Counties, North Carolina, it was found that the pure pyrophyllite contains small lenses of sericite, and that the two grade into each other.

The pure massive phases of the two minerals were often difficult to separate on inspection, and chemical analysis was resorted to in order to determine the amount of each in the mass.

In making the analyses it was found that the combined water of pyrophyllite was harder to drive off than that of the sericite, in fact by using the Penfield method, it was possible to get a loss of only 4% from the pyrophyllite. Ignition over the full heat of a bunsen burner for forty minutes did not give a constant weight, and ten minutes further heating over a blast lamp gave but 0.2 per cent additional loss.

It was therefore decided to try heating the minerals in a furnace.

Specimens of pure pyrophyllite and pure sericite, as determined by chemical analyses were selected and ground to pass a hundred mesh sieve. Porcelain crucibles of 10 ccm. capacity were heated to constant weight, and duplicate samples of pyrophyllite and sericite that varied from 0.9 to 1.1 grams were weighed out for each temperature used. These samples were heated in an electric furnace at 400°, 500°, 600°, 700°, and 750°C,

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[1] Recd. July 21, 1924.

and in a gas furnace at 800°, 900°, and 1000°C. The temperatures were determined with a recently calibrated thermo-electric pyrometer.

It was found that after 110°C there was no loss until between 300° and 400°C in the case of the sericite, and between 400° and 500°C with the pyrophyllite.

The ovens used could be opened and closed while hot, so the samples were treated as follows: The first set of samples was placed in the cold oven and heated to 400° and held there for fifteen minutes. While the first set of samples was being dehydrated the second set was heated in a drying oven at 130° to prevent the crucibles breaking when they were placed in the hot oven. As soon as the first set of samples had been heated at the required temperature for fifteen minutes it was removed, cooled in a desiccator and weighed at once, and the second set which had been heated in the drying oven was put into the furnace and heated at the next required temperature, while set number 3 was put into the drying oven to be heated to 130° and prepared for the furnace. In turn every set of samples was treated alike. It was found that 30 minutes time was required to raise the temperature from one stage to the next, hence, as the temperature was held at the pre-determined point for fifteen minutes every set of samples was in the furnace forty-five minutes, under approximately the same conditions except for the increase in temperature. The loss in the duplicate samples checked in every case within .07%.

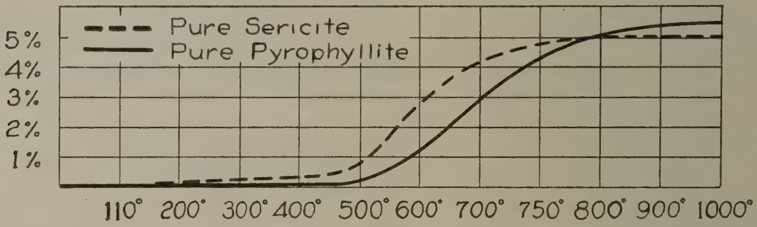

Fig. 1.

The diagrams given in Fig. 1 show graphically what happened.

The pure pyrophyllite and sericite have about the same percentage of water, although in this case the pyrophyllite had a small amount more water than the sericite.

Between 500° and 600° the sericite lost 2.2% while the pyrophyllite lost .98%, between 600° and 700° the sericite lost 1.35% while the pyrophyllite lost 1.84%, between 700° and 750° the sericite lost .39% while the pyrophyllite lost 1.47%, and between 750° and 800° the sericite lost .40% and the pyrophyllite .75%. At 800° the sericite was completely dehydrated while the pyrophyllite still had about .2% which was driven off at 900°.

The sericite showed a large percentage loss of water between 500° and

600° and after that the loss was gradual and uniform. The pyrophyllite showed its first permanent loss between 500° and 600° and its greatest single loss was between 600° and 700°, but as a whole the loss was more uniform and a higher temperature was required to completely dehydrate it.

It may be of interest in this connection to refer to some earlier work done by Le Chatelier.[1] He determined the points at which pyrophyllite loses its water by getting the points at which on rapid heating there was a retardation in temperature use, and found one at 700°C and another at 850°C. It will be noted, however, that from the present writer's experiments the pyrophyllite continued to lose water at a higher temperature than 850°C.

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[1] Soc. Min. France, *Bull.* **10**, 207 (1897).

DETERMINATION OF THE DISTRIBUTION OF HEAT IN KILNS FIRING CLAY WARES[1]

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ABSTRACT

This paper presents a description of some methods of collecting data on the performance of ceramic kilns and an explanation of the formulae used in calculating heat accounts from the data. It is hoped that these methods may serve as a foundation for the formulation of a code for testing kilns in order that the efficiency of new kilns can be determined on a comparative basis.

Introduction

The investigation of burning problems in refractory kilns included tests of seven kilns on each of which data were taken during two burns. The first burn on each kiln was conducted according to the usual plant practice while the second burn was conducted with changes which, it was thought, would reduce the burning time, reduce the coal consumption or improve the quality of the ware.

An important feature of the investigation was the collection of data from which the distribution of the heat input could be determined. This paper presents in detail the methods of collecting these data and the calculation of the heat accounts, and a discussion of the meaning of the various items. It was necessary in making the calculations to make certain assumptions which may not be absolutely correct; also it was impossible to determine certain heat losses. However, it has been possible to account for from 70 to 93% of the heat content of the fuel fired into the kilns tested. Had the tests been conducted for the sole purpose of making heat accounts it would have been possible to obtain additional data from which a closer accounting of the distribution of the total heat input could have been made.

The heat accounts which follow consist of fourteen items.

1. Heat used to raise the temperature of the brick.
2. Heat used to raise the temperature of the saggers.
3. Heat used to evaporate moisture from the brick.
4. Heat in combustible in ash.
5. Heat in combustible in flue gases.
6. Heat in dry flue gases.
7. Heat in water vapor in the flue gases formed from the coal.
8. Heat used to raise the temperature of the walls of the kiln.
9. Heat used to raise the temperature of the crown of the kiln.
10. Heat lost by radiation and convection from the walls of the kiln.
11. Heat lost by radiation and convection from the crown of the kiln.

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[1] Published by permission of the Director, U. S. Bureau of Mines. Recd. March 18, 1924. Released for publication by the Refractories Manufacturers Association, July, 1924.

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12. Heat given up by gases between bottom of kiln and stack.
13. Unaccounted for losses.
14. Total heat in coal fired.

Methods of Collecting Data and Calculation

The methods employed in collecting the data and computing the item of the heat account follow in detail:

Heat Used to Raise the Temperature of the Brick The quantity of heat used to raise the temperature of the ware from its initial temperature to its final temperature was calculated from (*a*) the total burned weight of the brick set in the kiln, (*b*) the rise in temperature above the initial temperature, and (*c*) the corresponding mean specific heat.

(*a*) The burned weight of the brick set in the kilns was obtained by keeping an accurate record of the number of pieces set and by weighing a number of samples of each different shape as the burned ware was removed from the kilns.

(*b*) The initial temperature of the ware was measured with a mercury thermometer as the kiln was being set. The final temperature was estimated by taking the mean of a number of temperatures measured with platinum-platinum rhodium thermocouples which were permanently placed at representative points in the bottom, middle, and top of the setting as the ware was being set in the kiln.

(*c*) The ratio of the amount of heat required to raise the temperature of a substance one degree to that required to raise the temperature of an equal mass of water one degree, usually from 14.5°C to 15.5°C, is called its *specific heat*. The *thermal capacity* of a substance between two temperatures t_1 and t_2 is the quantity of heat required to raise the temperature from t_1 to t_2. As the specific heat varies with the temperature the mean value between the temperatures considered must be taken for purposes of calculation.

Inasmuch as it has not been possible to make specific heat determinations on samples of the brick burned in the kilns tested it has been necessary to refer to such data on specific heats of refractory materials as has been published by other authorities.

For fire clay brick the specific heats are obtained from Mellor's[1] formula:

Mean specific heat $= 0.192 + 0.000033\ T$, where T is expressed in degrees Fahrenheit.

For silica brick the values are obtained by calculation from data given in the *Gas World*[2] for the diffusivity and conductivity of silica brick.

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[1] Wilson, Holdcroft and Mellor, "Specific Heats of Fire Brick at High Temperatures," *Trans. Ceram. Soc.* (Eng.), **12,** 279 (1912–1913).

[2] A. L. Green, "The Thermal Conductivity of Refractory Materials at High Temperatures," *The Gas World,* **13,** July 1 (1922).

From Fourier's linear diffusion equation may be obtained the equation:

$$\text{Thermal conductivity} = K\cdot C\cdot S, \text{ or } S = \frac{\text{Thermal conductivity}}{K\cdot C}$$

where K = diffusivity
C = apparent specific gravity
S = specific heat

The mean specific heats thus obtained are:

Temp. in °F t	Mean specific heat between 32°F and t°F
200	0.170
400	0.180
600	0.189
800	0.198
1000	0.208
1500	0.231
2000	0.255
2500	0.278

For magnesia brick the values given by E. Heyn[1] are used, as follows:

Temp. in °F t	Mean specific heat between 77°F and t°F
200	0.219
400	0.233
600	0.244
800	0.252
1000	0.257
1500	0.270
2000	0.282
2500	0.294

The formula for the computation of the heat used to raise the temperature of the brick is:

$H = W\cdot(t_2 - t_1)\cdot S$

where H = the heat used to raise the temperature of the brick
W = the burned weight of the brick
t_1 = the initial temperature of the brick
t_2 = the final temperature of the brick
S = the mean specific heat between t_1 and t_2.

Using Kiln 5, test A, as an example:

$H = W\cdot(t_2 - t_1)\cdot S$ t_2 = 2160°F
W = 448,427 lbs. S = 0.26
t_1 = 90°F

then $H = 448{,}427 \times 2070 \times 0.26 = 241{,}000{,}000$ B.t.u.

The total heat content of the coal fired = 1,451,000,000 B.t.u.

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[1] E. Heyn, "Thermal Conductivity of Refractory Building Materials," *Mitteilungen a. d. kgl., Materialprüfungsamt,* **32,** 185 (1914).

$\frac{241,000,000}{1,451,000,000} \times 100 = 16.6\%$ of the total heat input used to raise the temperature of the brick.

Heat Used to Raise the Temperature of the Saggers

Saggers, or protective boxing, were used in only one of the kilns tested, that one burning magnesite brick. They are made necessary by the fact that the magnesite brick have not sufficient physical strength to bear the load of setting one on top of the other. In the kiln in question the ratio of ware burned to protective boxing was one magnesite brick to two and one-half silica bricks. The silica brick used were second quality brick from a silica brick plant operated by the same company.

The quantity of heat required to raise the temperature of the saggers from initial to final temperature was calculated from, (*a*) the total weight of saggers in the kiln, (*b*) the rise in temperature above the initial temperature, and (*c*) the corresponding mean specific heat.

(*a*) The total weight of saggers in the kiln was obtained from the setting record.

(*b*) The rise in temperature above the initial temperature is the same as that of the ware.

(*c*) The mean specific heat was obtained in the manner previously outlined.

The formula used for the computation is:

$$H = W \cdot (t_2 - t_1) \cdot S$$

where H = the heat used to raise the temp. of the saggers, in B.t.u.
W = total weight of saggers in pounds
t_1 = initial temp. of saggers in degrees Fahrenheit
t_2 = final temp. of saggers in degrees Fahrenheit
S = mean sp. ht. of the saggers between t_1 and t_2.

Heat Used to Evaporate Moisture from the Brick

The quantity of heat required to evaporate the moisture from brick in kilns is a function of (*a*) the weight of moisture present in the brick as they were set and (*b*) the temperature at which the moisture left the kiln.

(*a*) The weight of mechanical water present in the brick as they were placed in the kiln was determined from the total weight and average moisture content of the ware set. The average percentage of moisture in the green ware was estimated by weighing ten pieces taken during the setting in order to obtain a fair average and drying to a constant weight at 212° to 230°F.

(*b*) The progress of water-smoking was followed by observing the change in weight of a brick at the bottom of the setting suspended from a sensitive balance on top of the crown by an alloy wire. The average temperature of the gases leaving the kiln at the stack from the beginning of the burn until the weight of the suspended brick became constant was assumed to be the mean temperature of the moisture evaporated from the ware.

The total heat content of one pound of water at the mean temperature of water-smoking was computed from Pier's formula:

$$h = 1058.68 + 0.44701t + 0.000{,}01541t^2 - 0.000{,}000{,}000{,}2432t^3 + 1.9 \times 10^{-12} \times t^4$$

where h represents the total heat of steam in B.t.u. per pound from 32°F and t represents the temperature in degrees Fahrenheit.

The heat used to evaporate one pound of water is equal to $h-(t_1-32)$. t_1 is the initial temperature of the ware.

The heat used to evaporate the moisture from the brick is then computed from the formula:

$$H = W \cdot [h-(t_1-32)]$$

in which H = the heat used to evaporate the moisture from the brick

W = weight of mechanical water.

For example, Kiln 5, test A:

Weight of green ware = 474,270 pounds

Moisture content = 3.82%

$W = 474{,}270 \times 0.0382 = 18{,}117$ lbs.

$t = 170$°F

$t_1 = 90$°F

$h = 1135$ B.t.u.

$h-(t_1-32) = 1077$

$$H = 18{,}117 \times 1077 = 19{,}512{,}009 \text{ B.t.u.}$$

Heat content of coal fired = 1,451,000,000 B.t.u.

$\frac{20{,}000{,}000}{1{,}451{,}000{,}000} \times 100 = 1.4\%$ of total heat input used to evaporate moisture.

Heat in Combustible in Ash

The loss of heat due to the removal of unburned carbonaceous material with the ash and refuse is computed by taking the product of the percentage of combustible in the ash and refuse, as determined by laboratory analysis, the total weight of ash and refuse removed, and the calorific value of the combustible, which is assumed to be pure carbon with a calorific value of 14,540 B.t.u. per pound.

$$H = 14{,}570 \times 0.289 \times 14{,}540 = 61{,}224{,}014 \text{ B.t.u.}$$

where H = heat in combustible in ash

Weight of ash and refuse removed = 14,570 lbs.

Combustible in ash and refuse = 28.9%

$\frac{61{,}000{,}000}{1{,}451{,}000{,}000} \times 100 = 4.2\%$ of total heat content of coal fired removed as combustible in ash and refuse.

Heat in Combustible in Flue Gases

Carbon monoxide was the only combustible gas determined in the flue gases. Owing to the large combustion chamber afforded by the kiln and to the mixing and catalytic action of the hot ware during high-fire the amount of combustible gas in the flue gases is small and is composed almost entirely of carbon monoxide. The quantity of heat lost due to the escape of carbon monoxide at the stack is computed from the formula:

$$H = \frac{CO}{CO_2 + CO} \times W \times C \times 10{,}150$$

where H = heat loss due to combustible in flue gases
CO = volume percentage of carbon monoxide in flue gas
CO_2 = volume percentage of carbon dioxide in flue gas
W = weight of coal fired
C = pounds of carbon in flue gas per pound of coal
10,150 = B.t.u. difference in the amount of heat evolved in the combustion of one pound of carbon to carbon monoxide and to carbon dioxide.

$\frac{CO}{CO_2 + CO}$ = the proportion by weight of carbon present in carbon monoxide.

The loss was computed by taking a summation of computations for short periods in order to minimize the error introduced by the large change in the mass of flue gas per pound of carbon burned from the beginning to the end of the burn. A specimen computation for the fifth 24-hour interval on Kiln 5, test A, follows:

$CO_2 = 12.9\%$ $W = 19{,}469$ pounds
$CO = 1.0\ \%$ $C = 0.615$

$$H = \frac{1.0}{13.9} \times 19{,}469 \times 0.615 \times 10{,}150 = 8{,}743{,}192 \text{ B.t.u.}$$

The sum of the combustible gas losses for the whole test is 77,000,000 B.t.u.

$$\frac{77{,}000{,}000}{1{,}450{,}000{,}000} \times 100 = 5.3\%$$ of the heat supplied in the coal lost in unburned combustible gas.

Heat in Dry Flue Gases

The largest amount of heat lost in burning ware in periodic kilns is that which is carried away as sensible heat in the dry flue gases. The actual amount of heat thus lost is a function of the mass and temperature of the gases leaving the kiln at the stack. The mass of gases was computed from the amount of coal burned and the hourly analyses of continuous gas samples drawn through a water-cooled tube from the base of the stack. The temperature of the gases was measured in the stack at the point of sampling. The computation of the loss is from the formula:

$$H = M \cdot S \cdot (t_2 - t_1)$$

where H = the sensible heat in the dry flue gas
M = the mass of flue gas

S = mean specific heat between t_1 and t_2
t_1 = temperature of air entering furnaces
t_2 = temperature of gas at stack

The mass of dry flue gas, M, is equal to the weight of carbon burned × the weight of dry gas per pound of carbon. The weight of carbon burned = (weight of coal × carbon content) — (weight of ash and refuse × combustible content).

E. g., Kiln 5, test A:

Weight of coal	= 124,006 lbs.
Carbon content of coal	= 64.9%
Weight of ash and refuse	= 14,570 lbs.

Weight of carbon burned = (124,006 × 0.649) − (14,570 × 0.289) = 76,271 pounds, and $\frac{76,271}{124,006}$ = 0.615 pounds of carbon burned per pound of coal.

The weight of dry gas per pound of carbon is obtained from the formula: $\frac{44CO_2 + 32O_2 + 28(CO + N_2)}{12(CO_2 + CO)}$, in which CO_2, O_2, CO and N_2 represent the volumetric percentages of carbon dioxide, oxygen, carbon monoxide, and nitrogen, respectively, in the flue gas and 44 is the molecular weight of carbon dioxide, 32 that of oxygen, 28 that of carbon monoxide and nitrogen, and 12 the atomic weight of carbon.

The values used for the mean specific heats of the gases were:

Temperature, t°F	Mean specific heat between 32°F and t°F
200	0.240
400	0.242
600	0.245
800	0.247
1000	0.250
1500	0.256
2000	0.262

These were computed, for average samples of flue gases from coal burning kilns, from Pier's formulae.[1]

To allow for the change in the rate of gas flow during the firing of a kiln the sensible heat in the dry gas was computed for short intervals and the results added to obtain the total loss for each test.

E. g., Kiln 5, test A, fifth 24-hour interval:

Weight of carbon = 11,973
Pounds of flue gas per pound of carbon = 18.9
Mean specific heat = 0.244
t_1 = 79°F
t_2 = 607°F
11,973 × 18.9 × 0.244 × 528 = 29,153,355 B.t.u.

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[1] Hütte, "Des Ingenieurs Taschenbuch," **1**, 484–6.

The sum of the loss due to the sensible heat in the dry flue gas for test 5A was 280,000,000 B.t.u. or $\frac{280,000,000}{1,451,000,000} \times 100 = 19.3\%$.

Heat in Water Vapor in the Flue Gases Formed from the Coal

There is an unavoidable loss of heat in the water vapor present as moisture in the coal and formed by the combustion of the hydrogen content. The amount of heat carried away by the moisture is computed from the formula:

$$H = W \cdot [h_t - (t_1 - 32)]$$

in which H = total heat lost
W = weight of water vapor
t = mean temperature of flue gas
t_1 = mean air temperature
h_t = total heat of steam at temperature "t"

The weight of water vapor per pound of coal is nine times weight of hydrogen in one pound of coal. This is based on the assumption that the total hydrogen content of the coal is present in the form of water or combines with oxygen upon burning to form water vapor.

The total heat of steam above 32°F is computed from Pier's formula previously stated.

The value of H for an entire burn is the summation of H_1 computed for short intervals in order to eliminate error due to widely varying rates of combustion during the burn.

Specimen computation, Kiln 5, test A, fifth 24-hour interval:

5.3% hydrogen in coal as received
$9 \times 0.053 = 0.477$ pounds of water vapor from one pound of coal
$W = 9287$ pounds $h_t = 1335$ B.t.u. per pound
$t = 607$°F $h_t - (t_1 - 32) = 1288$ B.t.u. per pound
$t_1 = 79$°F
$H_1 = 1288 \times 9287 = 11,961,656$ B.t.u.

For test 5A the total loss of heat in water vapor in the flue gases formed from the coal was 88,000,000 B.t.u. or $\frac{88,000,000}{1,451,000,000} \times 100 = 6.1\%$.

Heat Used to Raise the Temperature of the Walls and Crown of the Kiln

The heat used to raise the temperature of the masonry of the walls and crown of the kiln is a function of the weight of the masonry, its increase in temperature during the burn, and its specific heat.

The weight of the masonry was estimated from kiln drawings and from measurement of the kilns. The heat used to raise the temperature of the walls, includes the heat used to raise the temperature of the bag-walls and wickets.

The initial temperature of the masonry was assumed to be the same as the air temperature. The final temperature was computed from readings of a number of thermocouples inside the kiln, imbedded between courses of the masonry at different heights and on the surface. Figure 1 shows how thermocouples were placed in the wall of Kiln 5.

The amount of heat used to raise the temperature of the masonry is computed from the formula:

$$H = W \cdot (t_2 - t_1) \cdot S$$

where H = heat used to raise the temperature of the masonry
W = the weight of the masonry
t_1 = the initial temperature of the masonry
t_2 = the final temperature of the masonry
S = the mean specific heat between t_1 and t_2.

Using Kiln 5, test A, as an example:

1. Heat used to raise the temperature of the walls:

(1) Walls:

W = 313,750 lbs.
t_2 = 956°F
t_1 = 90°F
S = 0.22

$$H = 313{,}750 \times 866 \times 0.22 = 59{,}775{,}650 \text{ B.t.u.}$$

Heat used to raise the temperature of the wickets = 3,029,963 B.t.u.
Heat used to raise the temperature of the bag-walls = 17,155,125 B.t.u.
Total heat to raise the temperature of the walls = 79,960,738 B.t.u.

or $\dfrac{80{,}000{,}000}{1{,}451{,}000{,}000} = 5.5\%$ of heat input.

Heat Lost by Radiation and Convection from the Walls and Crown of the Kiln

In a furnace which is in continuous uniform operation there is established a condition of practically constant rate of heat flow through the walls. It is then possible to compute the quantity of heat which is conducted through the walls from the formula:

$$H = \frac{K}{d}(t_2 - t_1),$$

where H is the quantity of heat conducted per unit of area per unit of time, K is the conductivity of the material, d is the distance between the two points in the wall whose temperatures are t_1 and t_2. However, the formula cannot well be applied to the periodic kiln because it is not until the very end of the burn, if at all, that a condition of thermal equilibrium is reached. Starting with a cold kiln it is obvious that such a calculation would include some heat which does not at once leave the furnace walls but remains stored in them until the end of the burn. Further, up to the present time, it has been impossible to obtain values of K for the materials used in the construction of the kilns tested.

Since the heat lost through the walls could not be computed from the conductivity formula with the available data, separate formulae were employed for estimating the quantity of heat which was lost from the surfaces by radiation and convection.

The heat lost by radiation from the exposed surfaces of the kilns was computed from the average mean surface temperatures and the temperature of the surrounding objects receiving radiation, during short intervals. The loss was computed for short intervals on account of changing conditions as the burn progressed. The walls, wickets, and crowns, having different surface temperatures, were computed separately.

Copper-constantan thermocouples were connected to thin copper plates cemented to the kiln masonry at representative points. The temperatures of the plates were taken as the temperatures of the radiating surfaces. No attempt was made to estimate the large amount of heat radiated from the furnace openings.

The measurement of the temperature of all objects receiving heat from the kilns by radiation being impossible, it was assumed that all the surrounding objects were at air temperature. Some error was probably introduced by this assumption, it being unlikely that all the surroundings were at the temperature of the air. A further source of error lies in the fact that at the beginning of a burn a kiln may receive some radiated heat from the sun or from adjacent hot kilns.

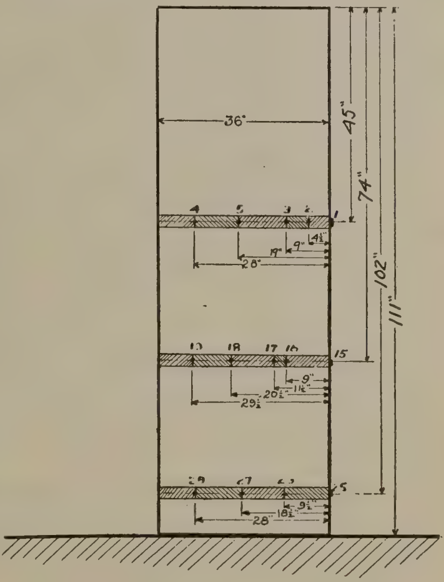

FIG. 1.—Section through kiln wall.

However, an idea of the magnitude of the heat losses from a periodic kiln by radiation and convection may be gained from computation based on Stefan's law. As stated by Langmuir,[1] Stefan's law is:

$$\text{Energy lost by radiation} = E \cdot \alpha \cdot (t_2^4 - t_1^4)$$

where E = emissivity constant

α = coefficient of total radiation

t_1 = temperature of surroundings (Absolute, deg. Cent.).

t_2 = temperature of radiating body (Absolute, deg. Cent.).

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[1] Irving Langmuir, "Convection and Radiation of Heat," American Electro-Chemical Society, April, 1913.

The emissivity constant, E, was assumed to be 0.90, that is, the kiln masonry emitted and absorbed 90% of black body radiation.

The value of the coefficient of total radiation[1] was taken as $\alpha = 5.7 \times 10^{-12}$ watt cm.$^{-2}$ deg.$^{-4}$. The factor 10^{-12} can be eliminated by substituting $\frac{t_1}{1000}$ and $\frac{t_2}{1000}$ for t_1 and t_2. Then substituting Fahrenheit temperatures and converting energy units to heat units:

$$H = 1543 \left[\frac{(t_2 + 460)^4}{1000} - \frac{(t_1 + 460)^4}{1000} \right] \text{ B.t.u. per square foot}$$

per hour.

where H = heat lost by radiation per unit surface per unit time
t_1 = air temperature in degrees Fahrenheit
t_2 = temperature of kiln surfaces in degrees Fahrenheit

Taking for an example the radiation from the walls of Kiln 5 during the fifth 24-hour interval, from the 97th to the 120th hour, inclusive, test A:

t_1 = 79°F
t_2 = 105°F
$H = 1543 \times 0.0175 = 27$ B.t.u. per sq. ft. per hour.
Area of walls = 1005 sq. ft.
Time = 24 hours

$27 \times 1005 \times 24 = 651{,}240$ B.t.u. lost by radiation from the walls during the interval.

The summation of similar calculations covering the entire test gives 7,000,000 B.t.u. lost from the walls, not including the wickets.

The quantity of heat lost by convection from the exposed surfaces was computed from the surface temperatures and the temperature of the surrounding air.

The formula used was from Langmuir:

Energy lost due to convection $= 0.000203(t_2 - t_1)^{5/4}$ watts cm.$^{-2}$

where t_1 and t_2 represent respectively the temperature of the air and the temperature of the hot surface, in degrees Centigrade. Substituting Fahrenheit temperatures and converting energy units to heat units the formula becomes:

$$H = 0.309(t_2 - t_1)^{5/4} \text{ B.t.u. per square foot per hour.}$$

The convection losses were computed for the same short intervals as were the radiation losses. The following specimen computation of convection loss from the walls is for the fifth 24-hour interval, Kiln 5, test A:

t_1 = 79°F
t_2 = 105°F
$t_2 - t_1$ = 26°F

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[1] W. W. Coblentz, "Constants of Spectral Radiation of a Uniformly Heated Inclosure or So-called Black Body, II," Bur. Stand., *Sci. Paper* **284**.

$H = 0.309 \times 25^{5/4} = 0.309 \times 58.711 = 18$ B.t.u. per sq. ft. per hour.

Area of walls = 1005 square feet.

Time = 24 hours

$18 \times 1005 \times 24 = 434{,}160$ B.t.u. lost by convection from the walls during the interval. The summation of calculated convection losses from the walls for the entire test gives 5,000,000 B.t.u.

No effort was made to make a correction for wind blowing over the kilns during the tests, so that the computed convection losses are probably lower than the actual convection losses. Also, no consideration was given to the shape of the kilns, which, no doubt, would make some difference in the magnitude of the losses.

The combined radiation and convection loss can be represented by combining the two formulae:

$$H = 1543 \left[\frac{(t_2 + 460)^4}{1000} - \frac{(t_1 + 460)^4}{1000}\right] + 0.309\ (t_2 - t_1)^{5/4} \text{ B.t.u. per}$$

square foot per hour.

For Kiln 5, test A, the combined radiation and convection loss from the walls and wickets was 1.0% and from the crown 4.4%.

Heat Given Up by Gases between Bottom of Kiln and Stack

The gases leaving a kiln give up a part of their heat content to the flues between the floor of the kiln and the base of the stack. The quantity of heat thus transferred from the hot gases to the masonry of the flues and foundations can be calculated. It is the difference between the heat content of the gases passing through the bottom of the kiln and the heat content of the gases entering the base of the stack.

The mass of gas passing through the bottom of the kiln was assumed in these calculations to be the same as at the base of the stack. The temperature at the floor was measured with platinum-platinum rhodium thermocouples. The sensible heat in the dry gases and the heat in the water vapor in the gases formed from the coal were computed for their temperature as they passed through the kiln floor. The computations were made by intervals in the same manner as the losses at the stack were computed.

For example, Kiln 5, test A:

At bottom:	Heat in dry gases	423,000,000 B.t.u.
	Heat in water vapor formed from coal	101,000,000 B.t.u.
	Total	524,000,000 B.t.u.
At stack:	Heat in dry gases	280,000,000 B.t.u.
	Heat in water vapor formed from coal	88,000,000 B.t.u.
	Total	368,000,000 B.t.u.

Heat given up by gases between bottom of kiln and stack = 156,000,000 B.t.u.

$$\text{Expressed in per cent of total heat input} = \frac{156{,}000{,}000}{1{,}451{,}000{,}000} \times 100 = 10.7\%$$

Unaccounted for Losses The difference between the total heat input and the sum of the computed losses is the unaccounted for loss. On Kiln 5, test A, the total heat input was 1,451,000,000 B.t.u. and the sum of the computed losses 1,112,000,000 B.t.u., a difference of 339,000,000 B.t.u., or 23.4% of the heat input unaccounted for.

Total Heat in Coal Fired The total heat content of the coal fired is the product of the weight of the coal fired and the calorific value of unit weight as determined by analysis of a representative sample.

Each load of coal delivered to a kiln was sampled and the 500 to 1000-pound sample which accumulated was crushed, mixed, and quartered until a two-pound sample remained for analysis. The samples were submitted to the Bureau of Mines laboratories for analysis.

Example, Kiln 5, test A:

Weight of coal = 124,006 pounds
Calorific value, as received = 11,700 B.t.u.
Total heat content = 124,006 × 11,700 = 1,450,870,200 B.t.u.

Discussion of Results

Table I gives the heat accounts in per cent of the total heat content of the coal fired for two burns on each of seven kilns burning refractory ware.

Heat Used to Raise the Temperature of the Brick In the refractories kilns the percentage of the total heat input used to raise the temperature of the brick varied from 13.2 to 27.7, except in the kiln burning magnesite brick where approximately 7% of the heat input was used to raise the temperature of the brick. However, including the 10 to 11% of the total heat input which was used to raise the temperature of the saggers in this kiln, the total percentage of the heat input which was used to raise the temperature of the setting was 17 to 18.

In the kiln burning silica brick 13.2 and 14.2% of the heat input was used to raise the temperature of the brick on two burns.

In five kilns burning fire-clay brick the heat used to raise the temperature of the brick varied from 15.7 to 27.7%. The highest percentages of heat used to raise the temperature of the brick were in Kiln 6, where two tests gave results of 26.3 and 27.7%. Kiln 6 was a comparatively small kiln with exceptionally large flues which facilitated its control. In addi-

TABLE I

HEAT ACCOUNTS OF REFRACTORY KILNS

Kiln number	Type of kiln	Inside dimensions	Number of furnaces	Grates	Number of stacks	Ware	Pounds of coal per thousand 9-inch equivalents for a number of preceding burns	Test	Duration in hours	Final temperature in degrees Fahrenheit	Pounds of coal per thousand 9-inch equivalents	Tons of coal per ton of ware
1	Round down draft	32 feet diam.	8	Horizontal	1	Magnesia	7940	A	157½	2460	6500	0.74
								B	157	2440	6640	0.69
2	Round down draft	38 feet diam.	8	Horizontal	1	Silica	4220	A	196½	2350	2560	0.32
								B	203¼	2530	2500	0.36
3	Round down draft	20 feet diam.	10	Horizontal	1	Fire clay	....	A	149½	2140	1270	0.20
								B	117	1980	1390	0.22
4	Rectangular down draft. "Newcastle"	30′6″ long x 16′6″ wide	6	Horizontal	1	Fire clay	1875	A	156	2140	1730	0.25
								B	134½	2230	1700	0.24
5	Round down draft	30 feet diam.	12	Sloping	1	Fire clay	2180	A	206½	2160	1940	0.28
								B	129	2210	1510	0.22
6	Round down draft	28 feet diam.	8	Sloping	1	Fire clay	1200	A	154½	2110	980	0.14
								B	114	2220	1070	0.15
7	Round down draft	25 feet diam.	10	Dead bottom	1	Fire clay	1513	A	83½	2150	1420	0.20
								B	80	2100	1370	0.20

TABLE I (*Continued*)

HEAT ACCOUNT IN PER CENT OF TOTAL HEAT INPUT

1 Heat used to raise the temperature of the brick	2 Heat used to raise the temperature of the saggers	3 Heat used to evaporate moisture from the brick	4 Heat in combustible in ash	5 Heat in combustible in flue gases	6 Heat in dry flue gases	7 Heat in water vapor in the flue gases formed from the coal	8 Heat used to raise the temperature of the walls of the kiln	9 Heat used to raise the temperature of the crown of the kiln	10 Heat lost by radiation and convection from the walls of the kiln	11 Heat lost by radiation and convection from the crown of the kiln	12 Heat given up by gases between bottom of kiln and stack	13 Unaccounted for losses obtained by difference	14 Total heat in coal fired
7.0	10.4	0.0	7.7	1.7	44.6	6.9	3.5	1.3	0.9	2.9	3.2	9.9	100.0
7.3	11.2	0.0	6.6	0.3	44.1	6.6	3.5	1.8	0.7	2.7	8.1	7.1	100.0
14.2	....	0.0	10.0	3.0	31.5	5.4	4.2	1.6	0.8	2.7	5.9	20.7	100.0
13.2	....	0.0	9.0	0.9	38.6	5.3	3.8	1.5	0.9	3.1	6.4	17.3	100.0
19.4	....	3.5	7.5	1.5	27.4	5.0	15.3	3.9	2.2	0.7	5.6	8.0	100.0
15.7	....	3.2	6.8	0.0	24.8	4.7	12.3	3.0	1.2	0.5	13.0	14.8	100.0
16.5	....	0.4	6.3	0.3	31.0	5.5	6.0	2.1	2.9	6.5	11.9	10.6	100.0
17.3	....	0.4	5.0	0.6	31.1	5.5	6.9	2.1	1.9	5.5	7.5	16.2	100.0
16.6	....	1.4	4.2	5.3	19.3	6.1	5.5	2.1	1.0	4.4	10.7	23.4	100.0
23.6	....	1.6	4.2	2.1	18.3	6.1	7.3	2.8	0.5	4.0	6.7	22.8	100.0
26.3	....	2.0	3.6	0.5	20.4	4.7	8.2	3.1	2.0	4.4	12.2	12.6	100.0
27.7	....	2.0	4.7	0.3	18.8	4.9	8.2	3.4	0.7	3.8	12.3	13.2	100.0
23.8	....	1.2	4.5	0.5	21.2	5.6	6.7	3.6	1.2	1.0	12.0	18.7	100.0
22.0	....	1.0	6.4	0.6	18.5	5.4	6.8	3.4	0.5	0.7	5.1	29.6	100.0

tion, the coal used had a high calorific value, its ash content was low, and there was a minimum of clinker formation. Results published by Navias[1] indicate that the quantity of heat required to burn clay ware is much greater than the thermal capacity of the burned brick. To make accurate heat accounts would, therefore, require determinations of the calorific values of each of the clays burned. If the figure 0.5 cal. per gram per degree C be assumed as the amount of heat required to burn the clay in Kiln 5 for example, the heat used to burn the brick becomes 32.0% for test A and 41.1% for test B.

Table II shows (1) the percentage of the total heat input required to burn the ware, using Navias' value, (2) the total percentage of heat accounted for when Navias' values are substituted for specific heat.

TABLE II

Kiln No.	Test	Heat used to burn the brick	Total heat account for
3	A	37.4	110.1
	B	31.0	100.5
4	A	31.7	104.6
	B	33.0	99.6
5	A	32.0	92.0
	B	41.1	94.6
6	A	50.4	111.5
	B	52.5	111.6
7	A	45.5	103.0
	B	42.4	90.8

The item—"heat used to raise the temperature of the brick"—may be termed "the heat stored up in the setting." Considering it as heat stored it becomes evident that in cooling the kiln a large part of this heat may be regained and diverted to other uses, thereby effecting a considerable economy in plant operation. The most apparent methods of using the heat stored in the ware are: (1) operation of driers, (2) generation of steam in waste-heat boilers, and (3) preheating air for combustion, as is done in continuous chamber kilns.

Heat Used to Raise the Temperature of the Saggers

Where a protective boxing is necessary for the protection of the ware which is being burned in a kiln, the material used for the protective boxing is heated to the same temperature as is the ware; a portion of the heat input is used to raise the temperature of the protective boxing.

For practical purposes the mean specific heat of the saggers and ware may be assumed to be the same; then, since both receive the same heat treatment, the ratio of the heat used to raise the temperature of the saggers to the heat used to raise the temperature of the ware is equal to the ratio of the weight of the saggers to the weight of the ware. Therefore, in the same kiln, the output of ware per unit weight of coal is greatest when the smallest possible mass of saggers is used. An additional advantage gained by reducing the ratio of saggers to ware is the increased production per kiln.

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[1] *Jour. Amer. Ceram. Soc.*, **6** [12], 1268 (1923).

In Kiln 1 a protective boxing was used. The ratio of the weight of protective boxing to the weight of ware burned was about 3 to 2 and the heat used to raise their temperature was in approximately the same ratio.

Heat Used to Evaporate Moisture from the Brick

In Kilns 1 and 2, burning magnesite and silica brick respectively, the ware was so dry when set in the kilns that less than $^1/_{10}$ of 1% of the heat input was required for the evaporation of the mechanical water.

In five kilns burning fire-clay brick the heat used to evaporate moisture varied from 0.4 to 3.5%. The results of these investigations indicate that with proper drier operation in the plant the removal of moisture from the ware in the kilns should not require more than 1% of the total heat input. The operation of driers was not included in the investigations.

No attempt has been made to estimate the quantity of heat required to remove the chemically combined water, owing to the lack of analyses and data on which to base computations.

Kiln Efficiency

The sum of the heat used to raise the temperature of the brick and the heat used to evaporate moisture from the brick may be used as an indication of the thermal efficiency of the kiln and furnaces. Kiln efficiencies obtained during the fourteen tests vary from 13.2 to 29.7%.

The efficiencies indicated by the tests on Kilns 1 and 2, burning magnesite and silica brick, are lower than those of the kilns burning fire-clay brick. It has been observed that the thermal efficiency of periodic kilns decreases as the ware is burned to higher temperatures. The efficiencies shown by the first two kilns are: test 1A, 17.5%; test 1B, 18.5%; test 2A, 14.2%; test 2B, 13.2%.

In these two kilns the brick were burned to approximately the same temperature. Several explanations may be offered for the higher efficiency of Kiln 1.

1. The thermal capacity of the magnesite brick burned in Kiln 1 is somewhat higher than that of the silica brick burned in Kiln 2.

2. The ware was not set as close in Kiln 1 as in Kiln 2. In general, the more accessible the surfaces of the ware are to hot gases and radiation from luminous flame and hot furnace walls the more readily will heat be transmitted to the surfaces of the ware.

3. The necessity of retarding the temperature rise in Kiln 2 to allow time for volume changes to take place in the silica brick undoubtedly lowered the efficiency of the kiln operation.

4. Kiln 1 was of better design and construction than Kiln 2, especially in the design of the furnaces and flues.

Kilns 3 and 4 are not comparable to any of the other kilns tested, owing to radical differences in design. Kiln 3 was a small round kiln, was originally an up-draft kiln and had been rebuilt to operate down-draft. Kiln 4 was a rectangular down-draft kiln of the "Newcastle" type, having a single flue across the bottom. Both of these gave lower efficiencies than other kilns burning fire-clay brick. Test 3A showed 22.9% efficiency; test 3B, 18.9%; test 4A, 16.9%; test 4B, 17.7%.

Kilns 5, 6 and 7 were all round, down-draft kilns burning fire-clay brick. Test 5A gave 18.0% efficiency; test 5B, 25.2%; test 6A, 28.3%; test 6B, 29.7%; test 7A, 25.0%; test 7B, 23.0%.

The increase of 7.2% in the efficiency of Kiln 5, in test B over test A, was due to improvements in setting and burning on test B, which materially decreased the burning time. During the water-smoking period on test B an induced draft fan was used in the stack which reduced the water-smoking period from 96 to 34 hours.

The high efficiency of Kiln 6 was due to the good construction of the flues and to the use of exceptionally high grade coal.

A fairly close approximation of kiln and furnace thermal efficiency may be easily made by any operator. The essentials are:

1. The calorific value of the coal.
2. A record of the weight of the coal used for firing the kiln.
3. The moisture content of the ware.
4. A setting record of the kiln.
5. A means of determining when water-smoking has been completed.
6. Means of measuring stack gas temperature.
7. Means of measuring temperature of ware.

Since the heat used to evaporate the moisture represents only a small part of the thermal efficiency, it may be disregarded, and a good idea of the efficiency had by determining only the percentage of heat used to raise the temperature of the ware. For comparative purposes the following formula may be used:

$$\text{Thermal efficiency of furnace and kiln} = \frac{W_B \times (t_2 - t_1) \times .26}{W_c \times C} \times 100$$

where W_B = burned weight of setting, in pounds
t_1 = initial temperature of ware, degrees F
t_2 = final temperature of ware, degrees F
0.26 = average value of mean specific heat of fire-clay brick in range $(t_2 - t_1)$

W_c = weight of coal fired
C = calorific value of coal, as received, in B.t.u. per lb.

The results of the last six tests indicate that efficiencies of over 20% are to be expected in the normal operation of round, down-draft kilns burning fire-clay refractories, with higher efficiencies attainable by careful and intelligent manipulation of the fires.

In burning periodic kilns comparatively high efficiency can be reached and maintained by supervision of the firing based on the study of temperature and draft measurements. It is suggested that with a thermometer, a pyrometer and a draft gage the operator can make a survey of his own burning conditions which will be found to be both interesting and profitable. Using charts, on which temperature and draft are plotted against time, in conjunction with records of the quality of ware produced and the quantity of coal consumed, faults in the existing burning schedule can be found and corrected.

The use of some type of nitrogen filled mercury thermometer is advised for studying kiln conditions during water-smoking, since the low temperatures of the water-smoking period are not easily read with accuracy on the charts of the high range pyrometers usually installed in kilns. The water-smoking thermometer may with advantage be placed in the lower part of the setting and withdrawn when a temperature of from 600° to 700°F is reached.

A pyrometer permanently placed inside the crown and as near the top as possible will give good data from which to prepare burning schedules. It has been found that pyrometers installed lower on the crown show temperatures too high and irregular, due to impinging flames.

The draft gage should be connected to the base of the stack. A connection to the bottom of the kiln is also desirable.

Heat in Combustible in Ash

For every kiln using coal as fuel a part of the total heat input is lost due to the removal of some combustible material with the ash and refuse. For the several kilns tested this loss varied from 3.6 to 10.0%.

In the case of the kilns for which the loss due to the removal of combustible with the ash was exceptionally large the coal as received contained a large proportion of fine material or was friable and broke up badly when handled and fired, so that the excess loss was traceable to the loss of fine coal through the grate bars during firing rather than to the removal of combustible from the furnaces during cleaning.

It is possible to reduce the amount of heat lost due to combustible matter in ash and refuse by careful manipulation of the fires, but since the heating up of the kiln would be retarded if the fires were allowed to burn out before the removal of the ash, the loss cannot be reduced to zero.

Heat in Combustible in Flue Gases

The fourteen tests showed carbon monoxide losses varying from 0.0 to 5.3%. With the exception of test 5A no kiln showed a loss of over 3% and in most cases the loss is under 1%. It has been shown by the investigation of the process of combustion in kilns that the gaseous products arising from the fuel beds are burned in the kiln almost immediately upon the admission of secondary air. Carbon monoxide passes through the kiln unburned only when no air is admitted above the fuel bed for its combustion. This condition is generally found in the first few minutes after firing when the firing openings are completely filled with coal. A careful fireman may reduce or eliminate this loss by leaving holes at the firing opening for some few minutes after firing, which procedure will also reduce the smoke evil.

Judgment should be exercised in making this attempt to reduce the carbon monoxide loss for if the openings are not closed within a short time after firing a greater loss will be introduced because of the admission of a large excess of air than was eliminated by the prevention of a deficiency of the air supply. Furthermore, if the reducing conditions are desired to bring out the color of the brick it must be paid for by this heat loss in the unburned carbon monoxide.

The loss due to the escape of combustible gas at the stack should not exceed 1% if the fires are properly handled, and, unless there are radical faults in the kiln construction, the method of setting the ware, or both, it need not exceed $^1/_2$ of 1%.

Heat in Dry Flue Gases

The largest single heat loss from periodic kilns is in the heat carried away by the dry flue gases, which, as has been explained, is a function of the mass of the gases per pound of coal fired and the temperature of the gases. Unless a regenerative system is used the temperature of the gases leaving the kiln must always be higher than that of the ware. The principal control of this loss must be, therefore, the control of the mass of gases per pound of coal or the excess air. The only definite method of determining the weight of the gases and the excess air is by means of analysis of the gases. Although the burning of kilns is rarely controlled by gas analysis it has been found, in general, that the ordinary plant practice maintained a reasonably low excess air, at least after the water-smoking period. This was accomplished without control apparatus because the flame temperature necessary to burn the ware cannot be attained with a low excess air.

The percentage of the heat input lost as sensible heat in dry flue gas varied between 18.3 and 44.6% for the seven kilns tested.

The highest flue gas losses occurred in the kilns burning ware to the highest temperatures, *i. e.*, the magnesite and silica brick kilns, which showed losses of from 30 to 45%. Approximately 20% of the heat input in the round down-draft kilns burning fire-clay brick was lost as sensible heat in the dry flue gases. It is this sensible heat in the dry flue gases which is most easily available for further use, such as the generation of steam in waste-heat boilers, operation of driers, and water-smoking other kilns. The economy accomplished by continuous chamber kilns is largely due to the use of the hot products of combustion for water-smoking and heating the ware in chambers ahead of those being fired.

Heat in Water Vapor in the Flue Gases Formed from the Coal

The quantity of heat lost in the water vapor in the flue gases formed from the coal is a function of two elements which are more or less the same in all kilns: (1) the hydrogen content of the coal, and (2) the temperature of the gases leaving the kiln.

The hydrogen content of the coal as shown by the ultimate analysis includes the hydrogen of the moisture in the coal and the hydrogen of the volatile combustible matter. Therefore, the loss may be reduced by avoiding the use of wet coal. It is scarcely necessary to add that the advantages of a high volatile coal are greater than the disadvantage of the increased loss in the heat in water vapor formed.

As would be expected, the percentage of heat loss from this source does not vary greatly. For the fourteen tests on refractories kilns the highest loss of heat in water vapor formed from the coal was 6.9% and the lowest loss was 4.7%. Reference to sixteen other tests shows this loss varying between the rather narrow limits of from 5 to 7%.

It should be noted that this loss does not accompany the combustion of coal only, but is encountered with practically all fuels. With natural gas it amounts to 11 to 14%; with fuel oil it is approximately 7%.

Heat Used to Raise the Temperature of the Walls and Crown of the Kiln

Expressed in thermal units the quantity of heat which is used to raise the temperature of the kiln masonry is proportional to the mass of masonry and its temperature. However, when expressed as percentage of the total heat input the figure is also effected by the ratio of the mass of the kiln masonry to the mass of ware burned. Kilns 1 and 2 were large kilns and the ratio of the mass of masonry to the mass of setting was small, so that, although the masonry was heated to higher temperatures than the masonry of the kilns in which fire-clay brick were burned, yet the percentage of the heat input used to raise the temperature of the walls and crown was comparatively low. Kiln 3 was an exceptionally small kiln having thick walls and a double crown; the ratio of the mass of masonry to the mass of ware set was high and the percentage of heat used to raise the temperature of the masonry was correspondingly high.

The percentage of the heat input used to raise the temperature of the crown did not vary greatly for different kilns, since all the crowns had about the same ratio to the mass of ware set. The volume of the crowns was small in comparison with the volume of the walls, but the percentages of the heat input used to raise the temperature of the crowns did not vary directly with the ratio of the mass of the crown to the mass of the walls because the temperature of the crown was always higher than that of the walls.

Heat Lost by Radiation and Convection from the Walls and Crown of the Kiln

It will be observed that in general the heat losses due to radiation and convection vary with the duration of the burn, but vary to a greater extent than the time. It has been shown[1] that during approximately the first one-third of a burn the heat which enters the walls is used almost entirely to raise their temperature and that but a small part of it reaches the surface to be lost by radiation and convection. Later, however, when the walls have been heated up, the heat which enters at the inside surface is practically all conducted to the outside surface to be lost by radiation and convection. It was observed on the seven refractories kilns that no exposed masonry surface ever reached a temperature higher than 350°F. Therefore, the length of time during which radiation and convection occur is a more important factor in radiation and convection from kilns than the temperature, since the temperatures of the radiating surfaces are always comparatively low.

On Kiln 1 the radiation and convection losses were lower for test B than for test A. The lengths of the two burns were the same; the temperature reached on the first burn was slightly higher than that reached on the second burn; a high soaking temperature was maintained on test A for a longer period than on test B.

Kiln 2 was the only kiln for which there were higher radiation and convection losses on the second test than on the first test. The second burn was longer than the first; a higher temperature was reached on the second burn.

On the remaining five kilns the radiation and convection losses were lower for the second burns because of shorter burning time. The losses from the walls were reduced somewhat by using $13^1/_2$-inch and 18-inch doors where it was the plant practice to use 9-inch doors.

In the losses by radiation and convection from the crowns it is of interest to note that the low loss from the crown of Kiln 3 was due to the fact that when the kiln was converted from an up-draft to a down-draft kiln, it was supplied with a double crown, the outer crown being separated from the inner crown by a 3-foot air space. The radiation and convection losses were computed from the outer crown.

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[1] R. T. Stull and John Blizard, "The Burning Problems of Industrial Kilns." Published by the joint Research Comm. of the four Heavy Clay Products Assns. in coöperation with the U. S. Bureau of Mines.

The crown of Kiln 7 was protected with a $2^1/_2$-inch course of insulating brick so that while the quantity of heat used to raise the temperature of the crown was somewhat high, due to the higher temperature of the firebrick under the insulation, the radiation and convection losses were lower than for larger uninsulated crowns.

Heat Given Up by Gases between Bottom of Kiln and Stack

This item, as previously explained, is the difference between the total heat in the gases at the bottom of the kiln, that is, the sum of the sensible heat in the dry gas and the heat in the moisture from the coal, and the total heat in the gases at the base of the stack. It is evident that this heat given up to the flue system serves no useful purpose except that if the gases did not give up this heat then more heat would be conducted from the hot setting through the masonry of the kiln bottom. Since the latter loss is not calculated the unaccounted for item would be larger.

The heat given up by the gases between the bottom of the kiln and the stack may, therefore, be added to the sensible heat in the dry flue gases, item 6, and the heat in the moisture formed from the coal, item 7, in order to obtain the total heat in the gases leaving the kiln.

There is considerable variation in the magnitude of this item for two tests on the same kiln. This is probably due to the fact that the temperature taken as the temperature of the gases leaving the bottom of the kiln was not representative. An accurate determination of the temperature of the gases at the bottom of the kiln would require a very extensive installation of thermocouples, whereas the temperature of the gases in the stack may be measured quite accurately by means of one thermocouple.

Unaccounted for Losses

The twelve preceding items account for from 70 to 93% of the heat input for the fourteen kilns tested.

The known sources of loss which have not been computed are:

1. Heat used to drive off chemically combined water in the ware.
2. Heat used to bring about chemical changes in the ware.
3. Heat used to heat moisture in the air used for combustion.
4. Heat lost by leakage of hot gases from kiln.
5. Heat loss due to rain falling on kiln and wind blowing over the kiln.
6. Heat conducted through the ground.

Heat Distribution at Various Periods of Burn

The heat accounts which have been presented cover the entire burn. It is obvious that because of changing conditions during the water-smoking, heating-up, oxidation, and soaking periods the heat fired into the kiln would not be distributed in the same manner during these different periods.

In order to learn how the distribution varied, heat accounts for tests A and B, Kiln 5, have been calculated for 24-hour periods. The results are given in Table III and are shown graphically in Fig. 2. The items have been grouped together in the figure so as to form five items.

The heat in the combustible in the ash could not be computed by periods and has thus been assumed to have been uniform during the entire burn.

The heat delivered to the ware which includes the heat to evaporate the mechanical water and the sensible heat stored in the ware is seen to have been about 26% during the first 24 hours, and to have reached a maximum of about 43% during the third period. From then on it decreased until during the last fourteen hours only $^1/_2$ of 1% of the heat in the fuel fired was taken up by the ware.

In the same manner the heat delivered to the masonry of the kiln decreased as the burn progressed but not as markedly since the difference

TABLE III

HEAT ACCOUNTS OF TESTS 5A AND 5B BY 24-HOUR PERIODS

Test No.	Period	Loss due to combustible in ash	Heat to evaporate mechanical water	Heat stored in ware	Heat stored in walls	Heat stored in crown	Heat given up by gases between bottom of kiln and stack	Sensible heat in dry stack gases	Heat in moisture in stack gases	Loss due to CO	Radiation and convection from walls	Radiation and convection from crown	Unaccounted for	Total
5A	1	4.2	6.4	20.0	3.4	3.2	0.7	1.1	4.3	0.0	0.2	0.6	55.9	100
	2	4.2	6.4	23.1	6.3	3.0	1.2	2.2	4.3	0.0	0.8	1.2	47.3	100
	3	4.2	6.4	36.3	9.5	4.3	4.1	3.0	4.4	0.9	0.6	1.4	24.9	100
	4	4.2	6.4	32.9	10.3	4.1	15.8	9.6	4.7	0.7	1.0	3.7	6.6	100
	5	4.2	0.0	29.0	8.4	3.6	11.9	12.8	5.2	3.8	0.7	3.2	17.2	100
	6	4.2	0.0	12.3	6.8	0.7	17.8	15.2	5.8	8.3	0.7	3.6	24.6	100
	7	4.2	0.0	6.7	4.8	1.4	15.0	24.1	6.6	7.8	1.2	5.6	22.6	100
	8	4.2	0.0	2.4	4.5	0.4	6.9	32.0	7.6	8.0	1.5	6.4	26.1	100
	9	4.2	0.0	0.5	2.3	0.3	4.3	40.0	8.0	2.9	2.3	7.8	27.4	100
Average		4.2	1.4	16.6	5.5	2.1	10.7	19.3	6.1	5.3	1.0	4.4	23.4	100
5B	1	4.2	9.9	25.9	6.1	3.9	1.1	3.1	4.4	0.0	0.1	0.2	41.1	100
	2	4.2	9.9[1]	36.2	9.0	5.3	3.5	8.1	4.8	1.6	0.1	1.1	16.2	100
	3	4.2	0.0	20.7	7.8	3.3	4.8	12.0	5.5	2.7	0.3	4.3	34.4	100
	4	4.2	0.0	15.2	7.3	10.6	13.3	18.7	6.3	1.7	0.6	5.8	16.3	100
	5	4.2	0.0	9.1	5.3	9.2	8.2	31.3	7.4	3.2	0.9	5.5	15.7	100
	6	4.2	0.0	4.0	3.4	5.8	4.3	37.4	8.1	1.9	1.3	6.2	23.4	100
Average		4.2	1.6	23.6	7.3	2.8	6.7	18.3	6.1	2.1	0.5	4.0	22.8	100

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[1] Water smoking complete at 34th hour.

between the temperature of the masonry and that of the gases was greater than the difference between the temperature of the ware and that of the gases.

The total heat in the gases leaving the bottom of the kiln which includes the sensible heat of the dry gases, the heat in the moisture in the gases, and the potential heat in the unburned gases is less than 10% during the first period but increases steadily during the burn until about 55% of the heat in the fuel fired is leaving the kiln in the gases.

The radiation and convection losses also increase as the burn progresses to a maximum of 10%.

That portion of the graph unshaded represents the unaccounted for losses which are noticeably very large during the early part of the burn. One of the most apparent explanations of this fact is that during the water-smoking period before the current of hot gases is established through the kiln a large part of the hot gases may be blown away from and not enter the kiln.

The remarks made concerning test A apply in general to test B also. This burn, however, was shorter than A by 77$^1/_2$ hours, a large part of this time being saved by decreasing the water-smoking period from 96 to 34 hours. In this way efficiency in the evaporation of the mechanical water was increased from 6.4 to 9.9% of the heat in the fuel fired during the water-smoking period.

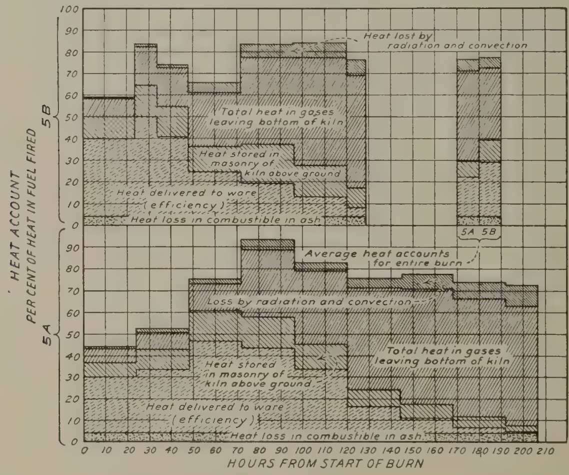

FIG. 2.

Although the heat lost in the gases leaving the kiln reaches a maximum comparable to that reached in test A, this high loss does not exist for so long a time and thus the average loss, as shown at the upper right, was about 10% less for test B than for test A. Similarly, the heat delivered to the ware was 7% greater for test B than for test A.

This chart shows clearly the advantage to be gained in the reduction of heat losses by shortening the time of the burn insofar as consistent with securing the proper quality of ware. A prolonged soaking period at the end of the burn is particularly undesirable for only a very small per cent of the heat is being efficiently used at this time.

Conclusion

The foregoing presents a description of some methods of collecting data on the performance of ceramic kilns and an explanation of the formulae used in calculating heat accounts from the data. It is hoped that these methods may serve as a foundation for the formulation of a code for testing kilns in order that the efficiency of new kilns can be determined on a comparative basis.

With the knowledge that every manufacturer of ceramic wares has not facilities for conducting similar complete tests on his kilns, short methods of approximating kiln efficiency and the more important heat losses have been given which can be easily applied on any plant.

The results presented cover several types and sizes of kilns and wares. They show with fair approximation the extent of the losses in these types of kilns. The value of these results lies principally in suggestions for the proper design of kilns. The heat losses in gases leaving the kiln and in heat used to raise the temperature of the kiln masonry point to economies to be expected in the different types of continuous kilns.

NOTE: The heat accounts which are presented herewith are taken from data obtained during an investigation of refractories burning problems by the United States Bureau of Mines and the Refractories Manufacturers Association's Committee to coöperate with the U. S. Bureau of Mines.

The writers wish to express their appreciation to G. A. Bole, superintendent of the Columbus Station of the Bureau of Mines, who directed and supervised the tests; to John Blizard, fuel engineer of the Bureau of Mines, who formulated the methods herein described; to C. E. Augustine, fuel engineer of the Bureau of Mines for assistance rendered; to W. D. Richardson, consulting engineer to the Bureau of Mines, for helpful suggestions; to the officials and men of the plants at which the tests were conducted for their kind coöperation; and to R. F. Lunger, A. W. Whitford, A. H. Fessler, E. M. Rupp, Franklin Wentzel, Jr., and W. T. Askin, of the crew of the Bureau of Mines Laboratory Car "Holmes," who assisted in collecting the data and computing the heat accounts.

THE ELECTRICAL RESISTIVITY OF REFRACTORIES[1]

By A. V. Henry[2]

ABSTRACT

The electrical resistivities of flint fire clay, kaolin, magnesite, sillimanite, silica, diaspore, Maryland, Italian and Indian talcs were determined at temperatures up to 1500°C. Tests were made in an atmosphere of nitrogen, by the Wheatstone bridge method, using 45-volt 1000 cycle alternating current.

With the exception of magnesite, the rate of decrease of resistivity decreases with an increase in temperature. The investigation indicates that the resistivity of a complex ceramic body, especially if it is open and porous, is not constant for a given temperature above the temperature at which its most fusible mixture melts. Resistivity is affected by the amount of impurities present, decreasing with an increase of impurities. As was shown in the tests of Italian talc, the resistivity is not only dependent upon the amount of impurities, but also upon their distribution. Within the limits of the voltage used, the resistivity is independent of the potential applied.

Introduction

The use of electrical energy as a source of heat has become widespread. In 1913, 131[3] electric furnaces were in operation in the metallurgical industry. This figure had increased to 875[4] in 1920. Today, 670,000[5] h. p. is consumed in the United States alone in developing heat for industrial purposes.

To meet the requirements of electric furnaces, it was necessary to develop special refractories whose properties include:

1. Ability to stand temperatures up to 1750°C.
2. Resistance to sudden temperature changes.
3. Resistance to chemical action.
4. Great mechanical strength.
5. High electrical resistivity.

The purpose of the following investigation is to determine the electrical resistivity of refractories, especially at high temperatures.

All electric furnace refractories are conductors of the second class and are therefore highly resistant to the passage of electric current at low temperatures. However, at high temperatures they become quite good conductors and are often responsible for a considerable current leakage between the electrodes of electric furnaces. In a test[1] conducted with a one-ton Stassano furnace operated at a voltage of 120, there was found to be a leakage of 300 amperes through the brickwork when the arc was interrupted. Efficient water cooling devices not only protect the electrodes but assist in keeping the electric leakage low by cooling the surrounding brickwork to a point where it is a poor conductor.

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[1] Published by Permission of the Director, Bureau of Mines. Presented at the Atlantic City Meeting, Feb., 1924.

[2] Fellow at Ohio State University working in coöperation with the Bureau of Mines.

[3] Rodenhauser and Schoenawa, "Electric Furnaces in the Iron and Steel Industry," p. 260.

[4] Robt. M. Keeney, "The Present Status of the Electric Furnace," *Chem. and Met. Eng.*, 980 (1920).

[5] B. S. Beech, "670,000 Horsepower of Electric Heat," *Industry Illustrated*, p. 21, Oct. (1923).

Electric heating appliances are generally constructed with the heating element wound on a ceramic base. It is essential that the base be a poor conductor at the maximum temperature at which the appliance is operated, to prevent an electrical short circuit through the base.

In some types of furnaces, refractories are used as resistors and as such are dependent on their ability to conduct electric current. The Baily[2] furnace is one of this type. It consists of a carborundum trough containing a granular carbon resistor. When in operation, the carborundum trough becomes a fair conductor and acts as an auxiliary resistor thereby lowering the current density in the granular carbon and also producing a more uniform heat.

The Nernst lamp is also dependent upon a ceramic mixture as a resistor. The electric filament consists of a mixture of magnesia and oxides of the rare earth metals which, when heated, will conduct sufficient current to keep it incandescent. Such resistors do not oxidize and therefore do not require a neutral or reducing atmosphere for successful operation. The development of a practical non-oxidizing resistor would be highly conducive to the further use of the electric furnace. It is therefore desirable to determine to what extent various refractories can conduct electric current.

Previous Investigations

Dr. E. F. Earhart[3] has made electrical conductivity tests on porcelain, applying a high potential direct current to the test pieces and at the same time measuring the current. From Ohm's Law, the resistance was computed. Pieces 2 cm. in diameter and 2 cm. long were molded and mounted between platinum tipped copper rods and the whole placed in a wire resistance electric furnace. Measurements were made up to 500°C. A reverse electromotive force was noted, having a magnitude which increased with time until the test potential was reached.

P. H. Brace[4] in similar tests with magnesia and porcelain, using direct current, observed the apparent specific resistivity to be dependent upon the duration of the application of the test current. At 990°C porcelain behaved as if it were a storage battery, producing a measurable current one-half hour after the test current had been disconnected.

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[1] Rodenhauser and Schoenawa, "Electric Furnaces in the Iron and Steel Industry," p. 101.

[2] H. W. Gillett, "Requirements of Refractories for Furnaces Melting Copper Alloys," *Jour. Amer. Ceram. Soc.*, **6** [4], 600 (1923).

[3] E. F. Earhart, "Notes on the Electrical Behavior of Porcelain and Glass at Moderately High Temperatures," *Ohio Jour. of Sci.*, **16**, 81 (1916).

[4] P. H. Brace, "Electrical Resistivity of Porcelain and Magnesia at High Temperatures," *Trans. Am. Electro-Chem. Soc.*, **33**, 205 (1918).

The Bureau of Standards[1] has developed a method of testing the resistivity of spark plug porcelains. This method is also based upon Ohm's Law. The test piece is molded in the form of a cup, 60 mm. in diameter, 65 mm. high and with walls 2.5 mm. thick. The cup is filled to a depth of 2 cm. with solder which forms one electrode. It is then placed in a shallow steel dish containing melted solder which forms the other electrode. Temperature measurements are made both of the solder in the test piece and of the solder in the shallow dish. When the desired temperature has been reached, the test piece is subjected to an alternating current of 60 cycles at 500 volts. The flow of current is then measured by means of a dynamometer milli-ammeter and the resistance calculated. This scheme has the advantage of giving a good electrical contact but is dependent upon the non-absorption of the metal by the test piece.

Dr. Northrup[2] gives a method for determining the resistivity of refractories at temperatures up to 1600°C. Good results were obtained with alundum cement and it is therefore recommended for similar work with other refractories. Alternating current was used for testing since it had been noted that direct current caused a counter electromotive force to be developed. Electric conduction in refractories is probably a combination of electronic and electrolytic conduction, making such measurements equivalent to the determination of the internal resistance of an electric battery. The test pieces were clamped between graphite plates, subjected to 120 volts alternating current and the resistance measured by means of an electrodynamometer. This method, in general, has been followed in the present investigation.

General Method

The refractories to be tested were made up into small tiles and clamped between graphite plates. The testing unit thus made, was suspended in a tube furnace the temperature of which was closely controlled by a rheostat. Electrical resistance measurements were made with a Wheatstone bridge using 45-volt 1000 cycle alternating current. Temperature measurements were obtained with a platinum-platinum rhodium thermocouple and readings taken up to and including 1500°C.

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[1] National Advisory Committee for Aeronautics. "Spark Plug Defects and Tests," *Rept.* **51.**

[2] E. F. Northrup, "High Temperature Resistivity of Refractories," *Met. & Chem. Eng.*, 123 (1914).

Apparatus

The electric furnace consists of an alundum core three inches in diameter and twelve inches long, wound with 34 feet of molybdenum wire 0.075 inch in diameter. The core has a pitch of four turns to the inch, thus giving a heating surface ten inches in length. The winding is embedded in alundum cement and the whole placed in a 12-inch steel shell and packed with dead-burned magnesite as shown in Fig. 1. A removable cover plate of steel, insulated with a heavy sheet of asbestos, is fastened to the flange at the top of the shell by means of four bolts. The alundum core is provided with a refractory cover. To prevent oxidation of the molybdenum wire, provision is made for passing nitrogen through the bottom of the furnace at the rate of one-half cubic foot per hour. The nitrogen proceeds from a tank into a calcium chloride bottle and through a flow meter. By calibration the differential pressure is measured in terms of cubic feet per hour. To remove any oxygen present, the nitrogen is passed through a quartz tube one inch in diameter and thirty inches long, containing copper clippings which are heated to 800°C by means of an auxiliary electric furnace. It then enters the furnace through an opening in the bottom. The testing unit and thermocouple are suspended in the furnace through an opening in the center of the top plate.

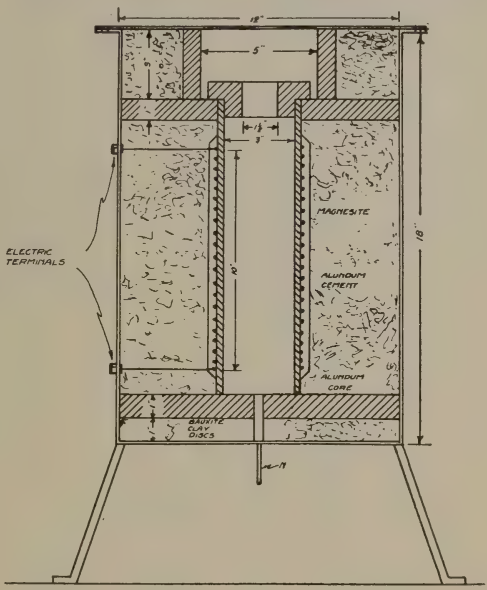
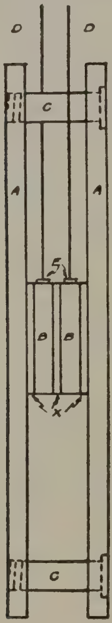


Fig. 1.—Molybdenum wound electric furnace.

The electric current for heating is taken from a 1- to 45-volt transformer for temperatures up to 1200°C. For higher temperatures, a water-copper sulphate rheostat is used in series with a 120-volt power line. To reach a temperature of 1500°C, 32 amperes at 120 volts are required.

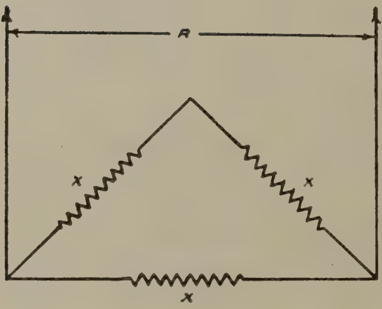
Testing Unit

Test Pieces.—In order to maintain a uniform structure in the refractories to be tested, the screen size, water content, and pressure to which the pieces were subjected when molded, were kept constant when possible. All materials were ground in an agate mortar to pass through a 150-mesh sieve, passed over an electromagnet to remove any free iron, and then tempered with 25% (absolute volume) of water. However, it was necessary to add additional water in some cases to safely mold the pieces and such additions are noted. Forming was done in a steel mold under a pressure of 6000 pounds per square inch giving tile $^1/_8$ inch thick, $1^3/_8$ inches wide and two inches long. Three pieces are required for testing. After being dried, all tile were burned twice in the electric test furnace to the maximum temperature to which they were to be tested. They were then dressed and measured, the thickness by means of a micrometer gage and the area by a polar planimeter. To insure good electrical contact, the surfaces of the pieces were coated with a thin layer of carbon black.



Testing Unit Legend

A—Graphite plates $^3/_8'' \times 1^3/_8'' \times 10''$
B—Graphite plates $^3/_8'' \times 1^3/_8'' \times 2''$
C—Graphite screws $^1/_2''$ (dia.) $\times 1^3/_4''$
D—Molybdenum terminals .075″ (dia.) $\times 10''$
E—Molybdenum plugs
X—Test pieces $^1/_8'' \times 1^3/_8'' \times 2''$



Theoretical Connections Testing Unit

Resistance (R) . . . . $= {}^{2x}/_{3}$
. . . . $x = {}^{3}/_{2}\,R$
ρ(sp. resistance) . . . . $= {}^{XA}/_{D}$
where A = area of test pieces
D = depth of test pieces
. . . . $x = {}^{\rho D}/_{A}$
Therefore . . . . ${}^{\rho D}/_{A} = {}^{3}/_{2}\,R$
And . . . . $\rho = {}^{3}/_{2}\,{}^{A}/_{D}\,R$

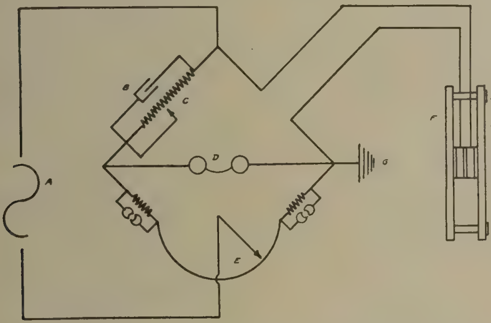
FIG. 2.

Graphite Plates.—The test pieces were clamped between four graphite plates, two of which are of the same width and length as the tile. The outer two are ten inches long and of the same width as the test pieces and all are $^3/_8$ inch thick. The 10-inch plates are bound together by two 1-inch graphite screws by means of which the pressure can be regulated. The assembly and theoretical connections are shown in Fig. 2.

Terminals.—Two molybdenum wires, 0.075 inch in diameter and ten inches long, were used as terminals. These were tapped into $^1/_4$-inch molybdenum plugs which were in turn tapped into the smaller graphite plates.

Temperature Measurements

Temperature readings were obtained with a platinum-platinum rhodium thermocouple in connection with a sensitive potentiometer. The couple was encased in a refractory protection tube and placed in the same position relative to the testing unit for all tests, so that any error due to a lag of temperature in the furnace, would be constant for all measurements. The cold junction of the couple was maintained constant by placing the ends and the leads in sealed glass tubes containing mercury and inserting them in a thermos bottle packed with ice. The maximum temperature at which resistance measurements were made was 1500° as this proved to be the practical limit for the thermocouple protection tubes.



Legend
A—Generator 1000-cycle a. c.
B—Variable condenser.
C—Variable resistance.
D—Telephone headset.
E—Slide wire.
F—Testing unit.
G—Ground.

FIG. 3.—Theoretical diagram of apparatus.

Resistivity Apparatus

The theoretical diagram of the apparatus used is shown in Fig. 3. The Wheatstone bridge consists of a[1] Kohlrausch slide wire (*E*), a 20,000 ohm variable resistance (*C*) and a telephone headset detector (*D*). The slide wire forms the variable ratio arms of the bridge. One end is connected to the variable resistance (*C*) and the other to the testing unit (*F*), while the remaining terminals of F and C are joined together. The telephone headset is connected, one end to the junctions of C and E and the other to that of F and E. The latter junction is grounded when working with high resistances. In order to balance out the capacity which is developed in all clays when subjected to an electric current, a variable condenser (B) is placed in parallel with the bridge arm (C). The condenser unit was made up of seven fixed mica condensers and one variable air condenser connected through a switchboard in such a way as to permit any capacity up to 0.15 microfarad to be obtained. The effect of a capacity in one arm of the bridge, is to throw out of agreement, the phase of the current flowing in that arm, as compared to the current flowing through the other arm. To obtain a null point or silence in the telephone headset, it is necessary to balance the capacity developed in the clays by an equivalent capacity from the condenser unit.

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[1] Leeds and Northrup, "The Measurement of Conductivity of Electrolytes."

The bridge has ten turns of wire upon its drum with a resistance of about 27 ohms and is provided with a scale having 2000 divisions. Readings, however, can be estimated to one part in 10,000 of slide wire. The wire is of sufficient size to withstand continued use without appreciable wear.

A 1000-cycle alternating current generator delivering 250 watts at 45 volts was used as the source of the exciting current. The generator was belt driven by a $^1/_4$-horsepower motor and was placed in a room beneath the laboratory so that the telephone detector could be used without interference. To prevent heating effects at contacts, the quantity of current used was kept at a minimum by placing a 20,000 ohm variable resistance in series with the generator leads.

Measurements

The testing unit was placed in the center of the furnace and since the effective length of the furnace is ten inches, uniform heating throughout the two inches of length of the test pieces was assured. The molybdenum terminals, after being screwed into the graphite plates, were connected to copper wire leads and through them to the bridge. The opening in the cover plate of the furnace, through which the molybdenum terminals extended, was sealed with asbestos sheeting and loose infusorial earth. This material acted as a short circuit across the terminals but as it was kept cool, its resistance compared to that of the test pieces was so high, that any error from this source was negligible.

When the desired temperature of the test pieces, as indicated by the thermocouple, was reached, the generator was started, thus causing an electric current to flow through the testing unit and the remaining arms of the bridge. By regulating the variable resistance C, and the capacity B, (Fig. 3) together with the ratio arms E, no current will flow through the telephone detector D. Under these conditions, the resistance of the testing unit multiplied by the length of the opposite ratio arm will equal the variable resistance multiplied by the length of the ratio arm opposite. In making readings, the ratio arms were maintained as nearly equal in length as possible and the exciting current was kept as low as was consistent with obtaining clear signals in the telephone detector. The mathematical derivation of the formula used after the resistance of the testing unit is obtained, follows:

If R = the resistance of the testing unit then $R = \frac{2X}{3}$
X = the resistance of each test piece $X = 3/2\,R$
P = Sp. resistance of the test pieces and $P = \frac{XA}{D}$
A = Area of test pieces $X = P\frac{D}{A}$
D = Depth of test pieces, therefore $P\frac{D}{A} = 3/2\,R$
and $P = 3/2\,\frac{AR}{D}$

Readings were taken at 100° intervals to 1500°C beginning at the lowest temperature at which accurate measurements could be taken.

Analysis of Method

All measurements were conducted in such a manner that any errors incident to the method would be constant throughout all tests. In making resistivity tests, the greatest difficulty lies in obtaining perfect contact between the electrodes and the test pieces. This was overcome by coating the pieces with a thin layer of carbon black by means of which the exciting current was distributed throughout the area of the pieces. Also, the area of electrical contact was large compared to the cubical content of the material tested. Since the test pieces were in contact with graphite, they were under reducing conditions, affecting most those materials containing iron compounds. The latter invariably had a lower resistivity under reducing conditions than when tested under oxidizing conditions. Any tendency for the deposition of carbon in the test pieces by the breaking down of any CO present was overcome by thoroughly reducing the materials and then heating them for four hours at 650°C under oxidizing conditions. At this temperature, any carbon present would be oxidized without affecting the status of the constituents of the test pieces. Any variation in temperature throughout the cross-section of the furnace was off-set by the fact that the pieces occupied only a relatively small volume of the furnace and were in contact with graphite which is a good thermal conductor. The thermocouple was placed adjacent to and touching the graphite plates. Since it was nearer to the heating element than was the testing unit, it was in a somewhat hotter part of the furnace. This was balanced, at least partially, by the lag in temperature through the thermocouple protection tube.

At low temperatures, the resistance of the materials tested is so high that the leakage of current through the condensers causes serious errors. Readings were taken at the lowest temperature at which the error due to this leakage was negligible. All measurements were checked by readjusting the test pieces and conducting a duplicate test. The absolute values of resistivity of the materials under the conditions by which tested is probably within 5% of the values given.

TABLE I—RESISTIVITY

Temp. in degrees C	Resistivity in ohms per centimeter cube				
	Flint fire clay	Kaolin	Sillimanite	Silica	Magnesite
300	660×10^4	133×10^5	....	....	....
400	729×10^3	145×10^4	358×10^5	828×10^5	....
500	140×10^3	269×10^3	607×10^4	113×10^5	....
600	422×10^2	747×10^2	148×10^4	236×10^4	....
700	158×10^2	302×10^2	467×10^3	775×10^3	....
800	701×10	146×10^2	179×10^3	300×10^3	330×10^5
900	353×10	744×10	739×10^2	117×10^3	116×10^5
1000	212×10	391×10	363×10^2	490×10^2	478×10^4
1100	147×10	235×10	179×10^2	259×10^2	848×10^3
1200	105×10	146×10	115×10^2	157×10^2	947×10^2
1300	864	106×10	572×10	111×10^2	141×10^2
1400	721	846	429×10	805×10	279×10
1500	582	681	315×10	566×10	615

TABLE II—RESISTIVITY

Temp. in degrees C	Resistivity in ohms per centimeter cube			
	Maryland talc	Italian talc	Indian talc	Diaspore
300	....	....	....	....
400	....	....	....	337×10^4
500	282×10^5	159×10^5	670×10^5	462×10^3
600	719×10^4	350×10^4	178×10^5	103×10^2
700	219×10^4	970×10^3	544×10^4	350×10^2
800	861×10^3	353×10^3	179×10^4	127×10^2
900	389×10^3	157×10^3	760×10^3	607×10
1000	238×10^3	749×10^2	340×10^3	292×10
1100	....	....	....	150×10
1200	....	....	....	886
1300	....	....	....	....
1400	....	....	....	....
1500	....	....	....	....

Flint Fire Clay

The flint fire clay used for testing is classified by the Ohio Geological Survey as No. 5825, Sciotoville clay and was mined in Scioto County, Ohio. It has a chemical composition as follows:

Moisture	1.35	TiO_2	1.80
Loss on ignition	12.90	K_2O	0.52
SiO_2	45.20	MnO	trace
Al_2O_3	36.77	Total carbon	0.25
Fe_2O_3	1.30	Inorganic carbon	0.03
CaO	0.50	P_2O_5	0.02
MgO	0.08	S	trace

It was ground to pass through a 150-mesh sieve and tempered with 10% water. The pieces were formed under a pressure of 6000 pounds per square inch and twice burned to 1500°C under the same conditions as when tested, giving a very hard dense body. A microscopic examination showed the burned pieces to be colloidal kaolinite anhydride together with small percentages of kaolinite anhydride and quartz crystals. The resistivity curve is shown in Fig. 4.

Kaolin

The kaolin tested was mined at Spruce Pine, North Carolina. It has the following chemical composition:

Hygroscopic water	3.07	TiO_2	0.03
Total water	16.83	CaO	trace
SiO_2	44.50	MgO	trace
Al_2O_3	37.55	K_2O	0.75
Fe_2O_3	0.54	Total	100.20

The kaolin was ground to pass 150-mesh sieve, tempered with 10% water and formed under a pressure of 6000 pounds per square inch. The pieces were twice burned in the electric testing furnace to a temperature of 1500°C giving a hard dense body. A microscopic examination of the burned body showed it to consist of aggregates of colloidal and crystalline kaolinite anhydride with an index of refraction of 1.57. The resistivity curve is shown in Fig. 5.

Sillimanite

A natural sillimanite, mined in the vicinity of Custer, S. D., was tested. It was ground to pass through a 150-mesh sieve, tempered with 8% of water and formed into tile under a pressure of 6000 pounds per square inch. The pieces were twice burned to 1500°C in the electric testing furnace, giving a hard dense body. A microscopic examination of the burned pieces showed the crystalline structure to be unchanged. The crystals, however, were somewhat stained due to the absorption of ferrous iron. The resistivity curve is shown in Fig. 6.

Silica

The silica tested was a Pennsylvania quartzite, finely ground, and used in the industry as potter's flint. It has the following chemical composition:

SiO_2	99.81	CaO	none
Al_2O_3	0.17	MgO	none
Fe_2O_3	0.014		

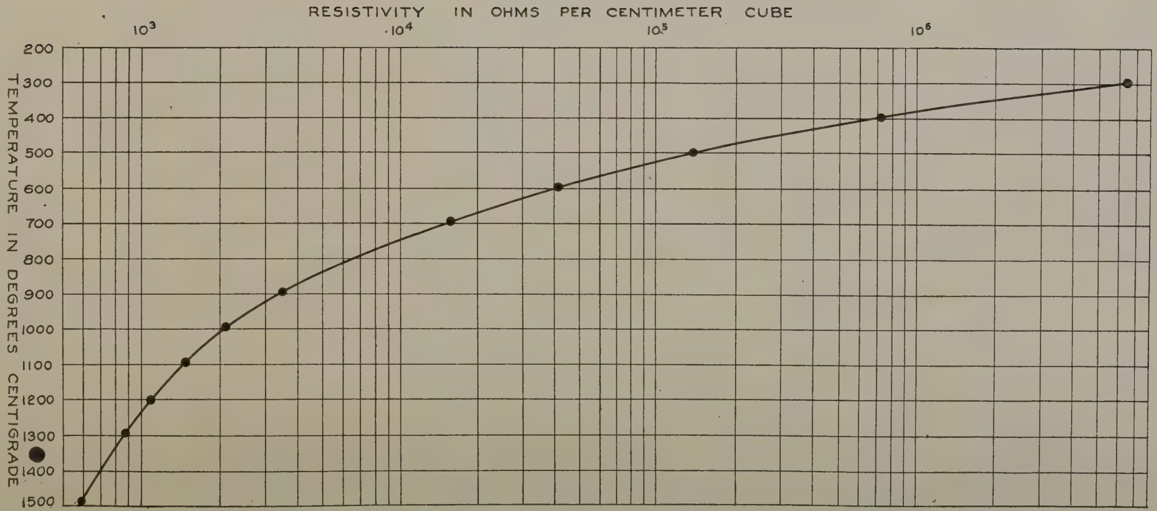

FIG. 4.—Flint Fire Clay.

Data: Test pieces tempered with 10% water by weight. Dry pressed under pressure of 5000 lbs. per square inch and twice fired to 1500 °C. Conductivity measurements made in an atmosphere of nitrogen with Wheatstone bridge using 1000-cycle alternating current. Test pieces in contact with graphite plates.

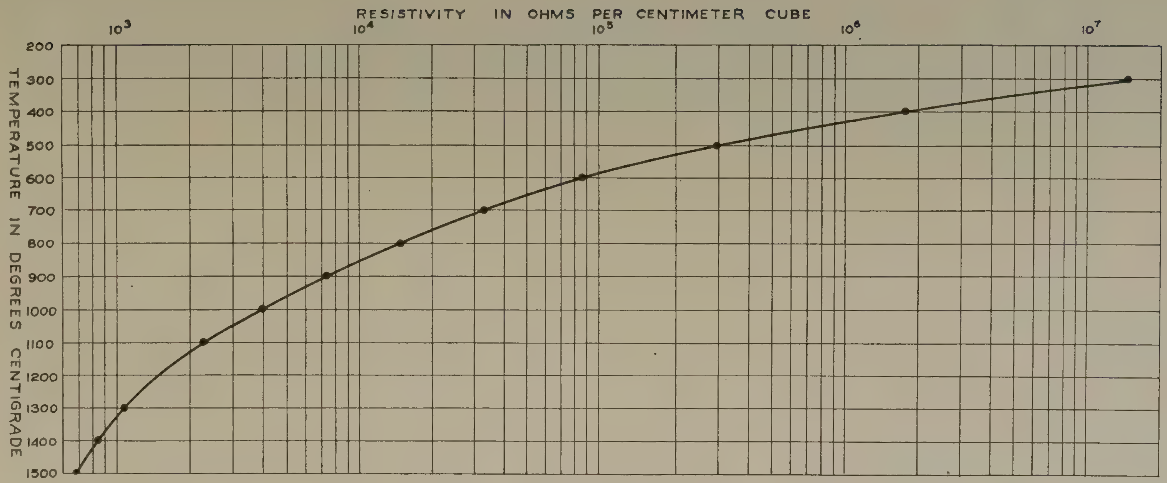

FIG. 5.—Kaolin (North Carolina).

Data: Test pieces tempered with 10% water by weight. Dry pressed under pressure of 6000 lbs. per square inch and twice fired to 1500°C. Conductivity measurements made in an atmosphere of nitrogen with Wheatstone bridge using 1000-cycle alternating current. Test pieces in contact with graphite plates.

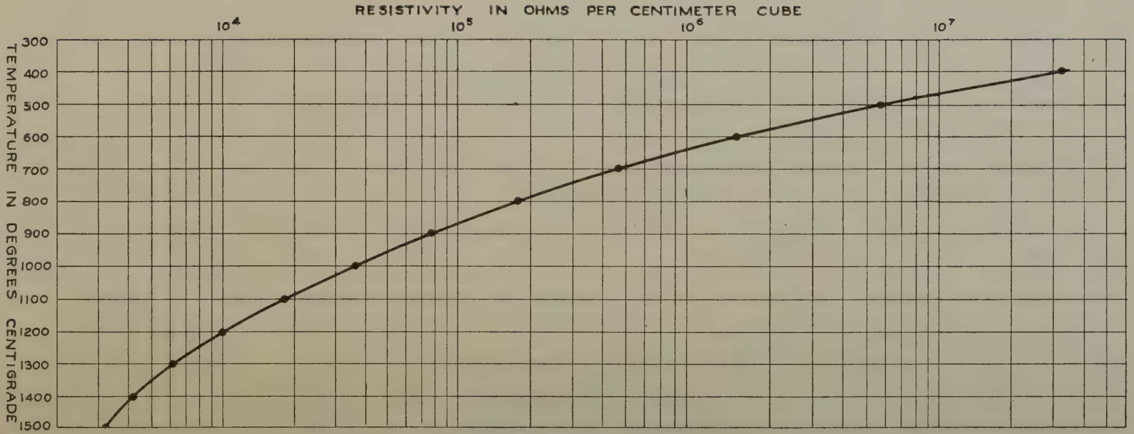

FIG. 6.—Sillimanite.

Data: Test pieces tempered with 8% water by weight. Dry pressed under pressure of 6000 lbs. per square inch and twice fired to 1500 °C. Conductivity measurements made in an atmosphere of nitrogen with Wheatstone bridge using 1000-cycle alternating current. Test pieces in contact with graphite plates.

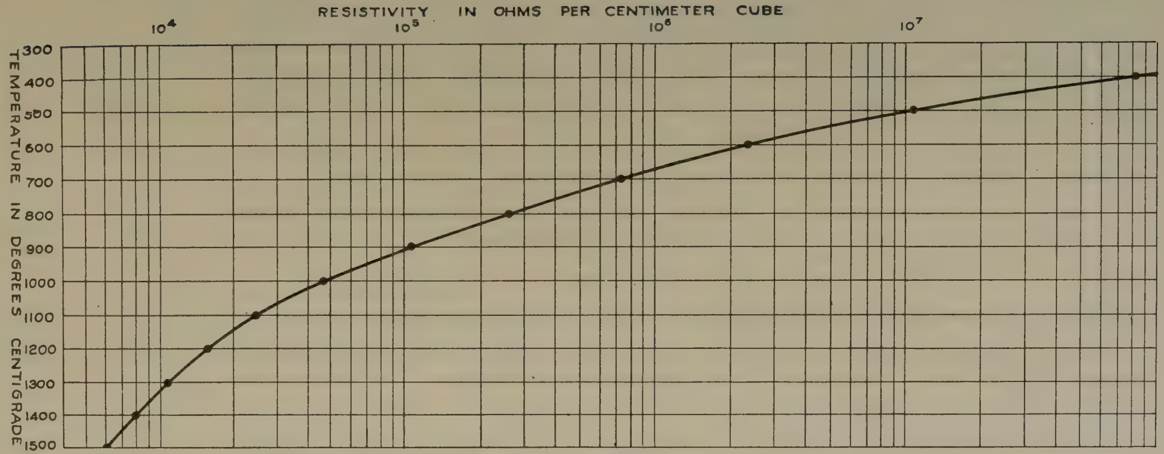

FIG. 7.—Silica (Potters Flint).

Data: Test pieces tempered with 17% water by weight. Dry pressed under pressure of 6000 lbs. per sq. inch and twice fired to 1500 °C. Conductivity measurements made in an atmosphere of nitrogen with Wheatstone bridge using 1000-cycle alternating current. Test pieces in contact with graphite plates.

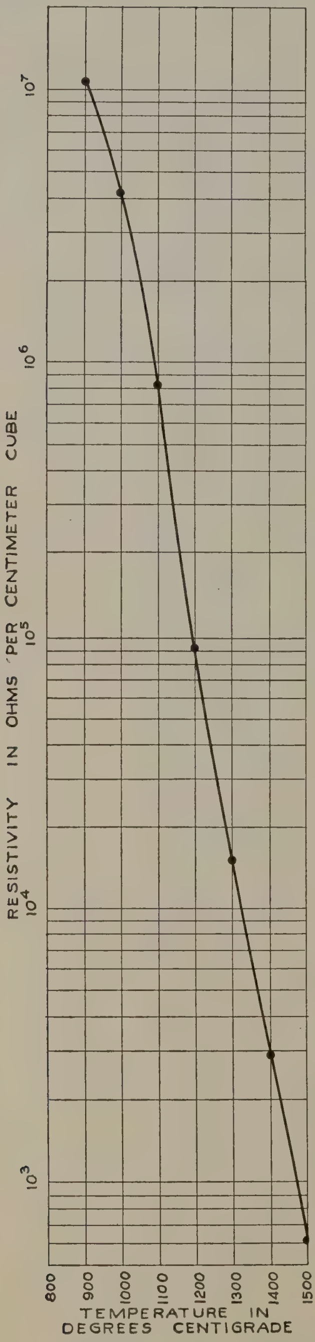

Fig. 8.—Magnesite (Austrian).

Data: Test pieces tempered with 30% water by weight. Dry pressed under pressure of 6000 lbs. per sq. inch and twice fired to 1500°C. Conductivity measurements made in an atmosphere of nitrogen with Wheatstone bridge using 1000-cycle alternating current. Test pieces in contact with graphite plates.

It was tempered with 17% of water, formed into tile under a pressure of 6000 pounds per square inch and twice burned at 1500°C in the electric testing furnace, giving a somewhat soft body. A microscopic examination showed the silica to be practically all cristobalite. The resistivity curve is shown in Fig. 7.

Magnesite

The magnesite used for testing was an Austrian magnesite. It was calcined to 1400°C, ground to pass through a 150-mesh sieve and tempered with 30% of water by weight. The test pieces were formed under a pressure of 6000 pounds per square inch, dried and twice burned to 1500°C, producing a hard dense body. A microscopic examination showed the burned body to consist of iron stained periclase crystals. The resistivity curve is shown in Fig. 8.

Talcs

Comparative tests were made on Maryland, Italian and Indian[1] talcs. Typical analyses[2] of these talcs are as follows:

	Maryland	Italian	Indian
SiO_2....	58.68	61.52	61.00
Al_2O_3...	3.75	0.84	2.12
Fe_2O_3...	Indeterminate	none	none
FeO....	5.52	1.27	1.74
MgO...	26.80	31.38	29.83
H_2O....	5.33	5.42	5.56

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[1] Furnished by the American Lava Corporation.

[2] "Higrade Talc for Gas Burners," Diller, Fairchild and Larsen, *Econ. Geol.*, **15**, 574–609.

The test pieces were cut from the raw massive talc and twice burned to 1000°C under the same conditions as when tested. Resistivity measurements were made up to and including 1000°C as pure talc bodies are rarely used at higher temperatures.

The Maryland talc pieces when burned in a reducing atmosphere are uniformly slate colored and when viewed under the microscope are seen to consist of iron stained crystalline aggregates with an average index of refraction of 1.63. The Italian talc pieces are not homogeneous. When burned in a reducing atmosphere, the Italian talc produces an iron spotted light gray body, composed of stained crystalline aggregates having an average index of refraction of 1.60. The Indian talc, when burned as above, produces a uniform light gray body, composed of slightly stained crys-

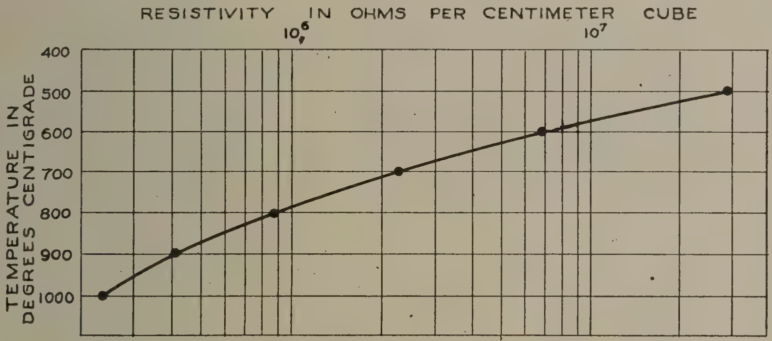

Fig. 9.—Talc (Maryland).

Data: Test pieces cut from raw talc block and twice fired to 1000°C. Conductivity measurements made in an atmosphere of nitrogen with Wheatstone bridge using 1000-cycle alternating current. Test pieces in contact with graphite plates.

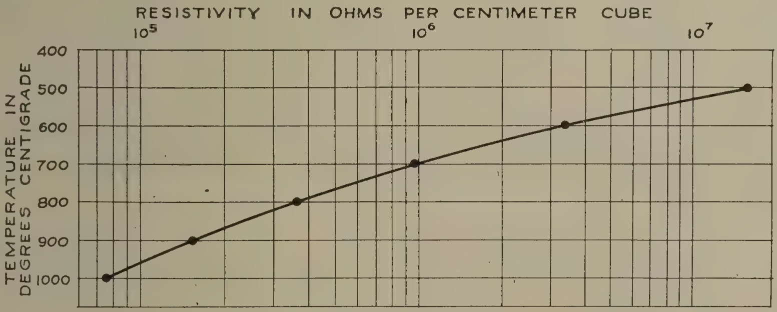

Fig. 10.—Talc (Italian).

Data: Test pieces cut from raw talc block and twice fired to 1000°C. Conductivity measurements made in an atmosphere of nitrogen with Wheatstone bridge using 1000-cycle alternating current. Test pieces in contact with graphite plates.

talline aggregates with an average index of refraction of 1.585. The Italian talc has the lowest resistivity due, no doubt, to the concentration of the iron and other impurities. If the talc had been pulverized and pieces molded, a much higher resistivity would probably have resulted. The resistivity curves are shown in Figs. 9, 10 and 11.

Diaspore

The diaspore used for testing was mined in the St. Louis district. It was ground to pass through a 150-mesh sieve and tempered with 9% of water by weight. The test pieces were formed under a pressure of 6000 pounds per square inch and twice burned to 1500°C producing a hard but somewhat porous body. When burned under oxidizing conditions, the resulting body is buff in color, while the reduced body is dark slate colored. A microscopic examination showed the reduced test pieces to consist of dark almost opaque crystalline aggregates. Resistivity measurements were carried through 1200°C. Above this temperature the resistance was not constant for any given temperature. A possible explanation is that at temperatures above 1200°C a eutectic is formed, producing a fluid mass in the porous body. Since the fluid mass has a certain freedom of movement, the structure does not remain constant.

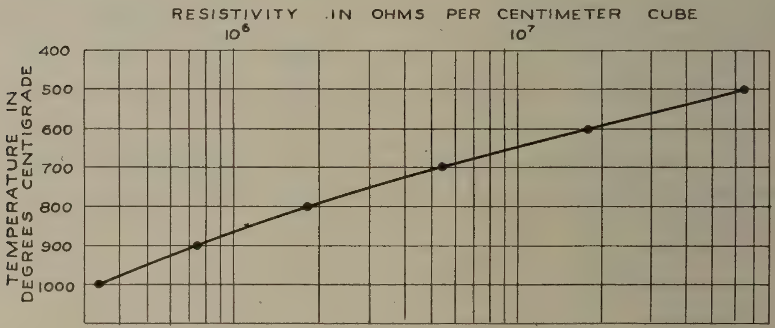

FIG. 11.—Talc (Indian).

Data: Test pieces cut from raw talc block and twice fired to 1000°C. Conductivity measurements made in an atmosphere of nitrogen with Wheatstone bridge using 1000-cycle alternating current. Test pieces in contact with graphite plates.

Conclusions

Of the materials tested, magnesite has the highest resistivity at low temperatures, while at high temperatures it falls almost to that of flint fire clay, which has the lowest resistivity at all temperatures. The kaolin curve lies parallel to that of flint fire clay, the lower resistivity of the latter being due in the main, to its higher percentage of fluxes. The resistivity of diaspore is higher than that of kaolin, with its curve being almost parallel to that of kaolin at the lower temperatures. The resistivity curve of sillimanite is of the same general nature although higher than those of flint fire clay, kaolin and diaspore.

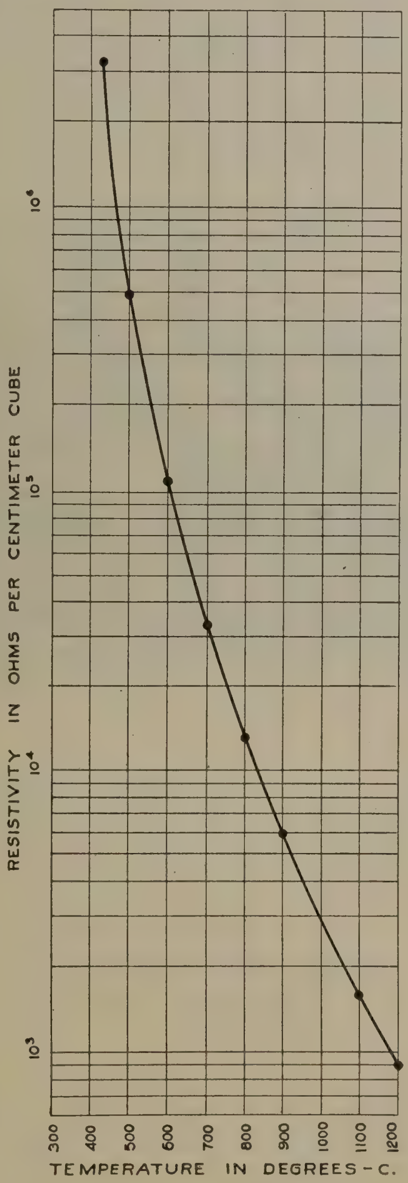

Fig. 12.—Diaspore.

Data: Test pieces tempered with 9% water by weight. Dry pressed under pressure of 6000 lbs. per sq. inch and twice fired at 1500°C. Conductivity measurements made in an atmosphere of nitrogen with Wheatstone bridge using 1000-cycle alternating current. Test pieces in contact with graphite plates.

It crosses the magnesite curve at 1375°C. The silica curve parallels that of sillimanite and crosses the magnesite curve at 1325°C. Indian, Maryland, and Italian talcs have high resistivities, the magnitudes of which are of the order as given.

With the exception of magnesite, the rate of decrease of resistivity decreases with an increase in temperature. The investigation indicates that the resistivity of a complex ceramic body, especially if it is open and porous, is not constant for a given temperature above the temperature at which its most fusible mixture melts. Resistivity is affected by the amount of impurities present, decreasing with an increase of impurities. As was shown in the test of Italian talc, the resistivity is not only dependent upon the amount of impurities but also upon their distribution. Within the limits of the voltage used, resistivity is independent of the potential applied. This is only true when the electrical contact between electrodes and the test piece is good.

Further Investigations

In order to determine any law governing the resistivity of ceramic bodies, it seems advisable to investigate the resistivity of uniformly varying mixtures of pure ceramic materials. While such an investigation would not approach commercial conditions, since pure materials would be used, it would furnish a basis for commercial practice.

The investigation was conducted under reducing conditions. Further tests of similar materials should be made under oxidizing conditions to determine what effect atmosphere has upon resistivity.

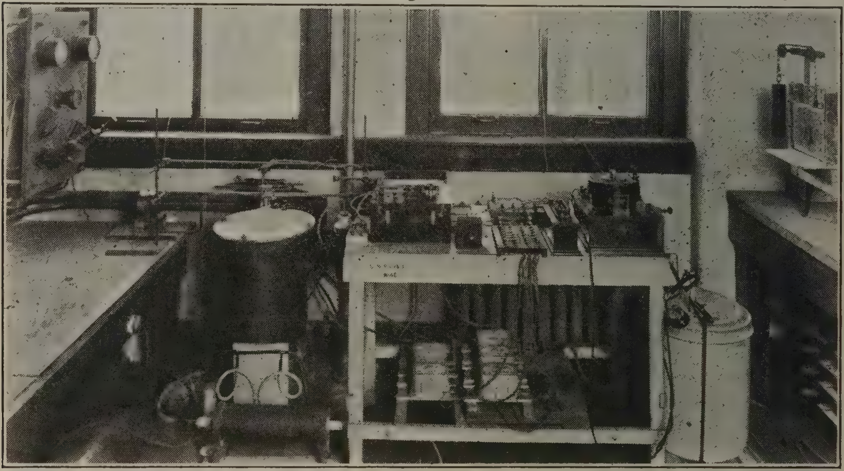

Fig. 13.

Resistivity measurements could, no doubt, be used to determine change of phase and eutectic formation in ceramic bodies. At the temperature where a change of phase occurred or a eutectic formed, there would be a sudden change in the slope of the resistivity curve.

Acknowledgment

The above investigation was conducted in coöperation with the Ceramic Experiment Station, Bureau of Mines. Acknowledgment is made for assistance given by A. S. Watts and G. A. Bole.

THE DESIGN OF KILNS AND FURNACES FROM MODEL TESTS[1]

By F. H. Norton[2]

Introduction

Many cases occur in engineering practice where the performance of a large and expensive structure cannot be calculated in advance because of the extreme complication of the governing laws.

Perhaps the most notable example of this kind is ships' hulls, where a model is resorted to for producing the form of lowest resistance fitting the given conditions and to predict the performance of the full-sized ship. By the use of now well established correction factors, the full scale performance can be determined with remarkable precision.

More recently aerodynamic models have been used to a great extent to develop more efficient shapes and to predict the performance and stability of airplanes. It is considered very hazardous to fly a new type of airplane until the model test has proved satisfactory.

Mechanical models are often used for measuring stresses in complex structures by the photo-elastic method and have proved of great value.

There have been recently constructed a number of kilns of new design and of considerable cost (such as tunnel kilns) which have required long and costly alterations from the original plans before satisfactory operation could be established. If it were possible to construct a model of the proposed kiln and first carry out the experimentation on it—and yet be certain that the large structure would simulate the performance of the model—a great saving in time and money would be made.

It is undertaken here to analyze the effect of scale on gas and heat flow and to determine the possibilities and limitations of using models.

Dimensional Analysis

It is necessary to utilize the greatest care in interpreting the results of model tests, or erroneous conclusions may result. Therefore it is advisable to apply, where possible, the principle of dimensional analysis, which is really quite simple in its application, as indicated below.

All physical quantities can be expressed as functions of these fundamental units,

Quantity	Symbol
Length	L
Time	T
Mass	M
Temperature	θ
Heat quantity	H

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[1] Recd. Sept. 12, 1924.

[2] Babcock and Wilcox Research Fellow, Division of Industrial Coöperation and Research, Mass. Institute of Technology.

Thus,

Velocity $v = LT^{-1}$
Acceleration $a = LT^{-2}$
Force $F = MLT^{-2}$
Energy $E = ML^2T^{-2}$
Density $\rho = ML^{-3}$
Heat quantity $H = L^3\theta = ML^2T^{-2}$
Conductivity $K = HT^{-1}L^{-1}\theta^{-1} = MT^{-2}L\theta^{-1}$
Specific heat $C = HL^{-3}\theta^{-1} = ML^{-1}T^{-1}\theta^{-1}$
Viscosity $\mu = ML^{-1}T^{-1}$
Kinematic viscosity $\nu = L^2T^{-1}$
Rate of heat transfer $h = HT^{-1} = ML^2T^{-3}$, etc.

As an example of dimensional analysis, let us determine in what way the resistance of a solid body in a moving fluid varies with changes in all quantities that can effect it. Let us list these quantities,

Quantity	Symbol	Dimensions
Length	l	L
Time	t	T
Velocity	v	LT^{-1}
Resistance	R	MLT^{-2}
Density of fluid	ρ	ML^{-3}
Viscosity of fluid	μ	$ML^{-1}T^{-1}$
Elasticity of solid	E	$ML^{-1}T^{-2}$
Velocity of sound in fluid	Q	LT^{-1} (compressibility of fluid)
Acceleration of gravity	a	LT^{-2}

Obviously the resistance will depend principally on l, v and ρ. So setting $R \infty l, v, \rho$ and substituting their dimensions, we get,

$$MLT^{-2} = L^a, L^b, T^{-b}, M^cL^{-3c}$$

Solving for a, b and c,

$$\begin{array}{rcl@{\qquad}rcl} 1 &=& a+b-3c & a &=& 2 \\ 1 &=& c & b &=& 2 \\ -2 &=& -b & c &=& 1 \end{array}$$

or $R \infty l^2v^2$, or $\left[\dfrac{R}{l^2v^2\rho}\right]$ is one of the six dimensionless products obtainable from the nine quantities.

Next assume that R is held constant and that μ varies in some way as $lv\rho$. As before the dimensionless product is obtained and is $\left[\dfrac{\mu}{lv\rho}\right]$. In the same way all the other quantities are equated to $lv\rho$ in turn so that there is finally obtained the following expression, where ϕ is an unknown function.

$$R = l^2v^2\rho\cdot\phi\left\{\left[\frac{\mu}{lv\rho}\right]\left[\frac{vt}{l}\right]\left[\frac{la}{v^2}\right]\left[\frac{E}{\rho v^2}\right]\left[\frac{v}{Q}\right]\right\}$$

This expression shows that the resistance of a body is proportional to l^2, v^2 and ρ if the five dimensionless products are held constant. That is if ρ and μ are the same for model and full scale the product of length and velocity must be constant and so on for the other products. It can be seen at once that it is impossible to vary l and keep all the products constant, therefore a model cannot exactly duplicate the full scale conditions.

Fortunately, however, by properly setting our limits, most of the dimensionless products can be safely neglected. For example, up to speeds of 600 ft./sec. the compressibility of the fluid (air) can be neglected, and the rigidity of the solid is unimportant except for flexible members like propeller blades. Also we may neglect acceleration and time with total immersion which leaves,

$$R = l^2 v^2 \rho \cdot \phi \left[\frac{\mu}{lvp} \right]$$

as the equation that will satisfactorily express the relation between model and full scale for any gas flow that will interest us.

The function ϕ can only be determined by experiment. While it is nearly constant over a large range at high values of vl, it changes rapidly at the lower limit of turbulent flow.

Gas Flow and Pressures

It has been previously shown that the resistance,

$$R = v^2 l^2 \rho \cdot \phi \left[\frac{\mu}{vl\rho} \right].$$

In the kiln the fluid travels through a passage and the drop in pressure P is desired. R in the above equation will evidently be replaced by $P \left[\frac{\pi}{4} \right] l^2$.

Then,

$$P = v^2 \rho \cdot \phi \left[\frac{\mu}{vl\rho} \right]$$

which is a relation well tested in experimental hydrodynamics.

For example, suppose the model is $^1/_5$ full size and that it is run with an average temperature of 240°F and the full scale kiln is operated at 2400°F and is supplied with 3500 cu. ft. of air a minute. First the velocity in the model must be chosen to make $\left[\frac{\mu}{vl\rho} \right]$ the same in both cases. To do this, the density and viscosity of air and combustion gas must be known for various temperatures. Unfortunately there is no such data available at the higher temperatures, but the values are exterpolated from the existing data as well as possible. (Fig. 1.)

The values of l, μ, v and ρ are:

	Model	Full scale	Ratio
Temp.	240 °F	2400 °F	10
l	$^1/_5$	1	5
ρ	93×10^5	20×10^5	.21
μ	230×10^6	490×10^6	2.1
v	11,700	23,400	2.0

The velocity for full scale is found by multiplying the velocity of the cold air by 6.1 (the ratio of the density at 60 °F and 2400 °F) for the volume increases immediately after passing through the burner. The velocity is that corresponding to all the hot gases passing through a one square foot section. On the model the velocity would be that of the air passing through an equivalent section, or $^1/_{25}$ of a sq. ft. The model v will evidently be 11,700 to make $\left[\dfrac{\mu}{vl\rho}\right]$ a constant, or the model need be run at only one-half the full scale velocity.

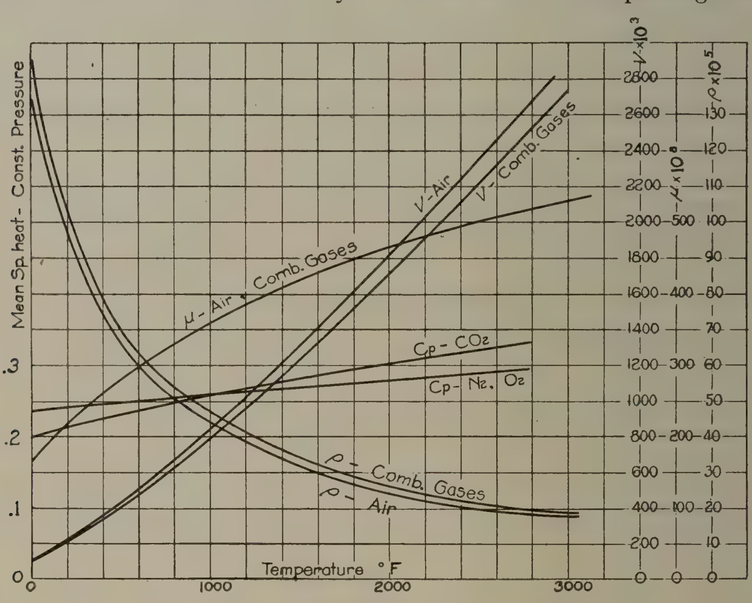

FIG. 1.

It should be noted here that the model kiln at low temperatures has an immense advantage over aerodynamic models in that the model velocity can be less than the full scale velocity. With the usual aerodynamic model of $^1/_{20}$ scale, the tests should be conducted at twenty times the full scale velocity to obtain similar flows for the air is the same in both cases. Such velocities, of several thousand miles an hour, are of course impractical and so these model tests require a correction factor of rather uncertain magnitude. It may be interesting to note that recently arrangements have been made to run aerodynamic models in air compressed to twenty atmospheres so that the corresponding speeds are the same.

Returning to the example, it is seen that the ratio of velocities is 2.0 and densities, .21. As $p = \rho v^2$, the pressure drop in any place in the model will be,

$$\frac{1}{.21} \times \left[\frac{1}{2.0}\right]^2 = 4.8 \times .25 = 1.2$$

times the pressure drop at the same place in the large kiln.

It should be noted that these pressures are only the pressures due to the motion of the gas and that there is another component due to the static head of gases in the kiln. This pressure is easy to compute from the density of the gases and the head. However, if the model is run at such a temperature that (ρl) is a constant, the model pressures will correspond to the full-sized ones. A $^1/_5$ size model run at about 300°F will fulfill this condition of similitude.

As the gas velocity in models is rather high and the stack short, it is always necessary to apply induced draft. This makes it impossible to determine directly from the model the operation of the stack. However, after the draft necessary is determined from the model, the height of the stack can be computed accurately as the friction loss in the stack is known.

It is perhaps well to call attention here to the necessity of correcting the pressure readings in the kiln for the atmospheric pressure gradient. Suppose pressure readings are taken in the top and bottom of the kiln as shown in Fig. 2.

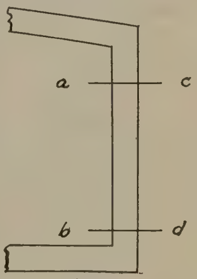

Fig. 2.

The first measurement will indicate *a-c* and the second *b-d* and the assumption is usually made that *d-c* is zero. The atmosphere gradient is 0.015 inch of water per foot, so that if *c* and *d* are 6 ft. apart, we have,

$$(a\text{-}c) - (b\text{-}d) = p_1$$
$$(a\text{-}b) - (d\text{-}c) = p_1$$
$$(a\text{-}b) = p_1 - (d\text{-}c) = p_1 - .09''.$$

It is quite possible to have a measured pressure at (*a*) less than at (*b*) and yet be forcing the gases downward through the charge. The position of the manometer in no way affects the readings if the tubes are filled with air at atmospheric pressure and temperature.

Heat Transfer

Heat may be transferred in three ways: by convection, conduction and radiation. These three methods vary with change of scale and temperatures in different ways so that a model that gives similitude in all of them is complicated. It is therefore quite desirable to know which is the most important.

The charge of bricks is the portion of the kiln of most interest, therefore the heat transfer will be computed there for actual conditions. Let Fig. 3 represent a section of the kiln, and assume a vertical temperature gradient of 1°F/cm. The temperature of the charge is 2400°F at *yy* and the gas temperature averages 2500°F and is traveling at a velocity of 100 ft./min.

The heat received by a surface from a moving gas has been measured at low and moderate temperatures and is given by:

$H = KTV$
$K = .000000434$ when T is in °C and V in ft./min.
H is in cal./sq. cm./sec.

Consider the section of one bench in Fig. 3 one cm. thick and running one cm. across the kiln. There will be two square cm. of surface exposed.

$$H = .000000434 \times 55 \times 100 = .0023 \text{ cal./sq. cm./sec. or for 2 surfaces, } .0046.$$

The heat given to this volume by conduction will evidently be the amount received from the top minus the amount passing out at the bottom. The heat flowing downward is 0.0040 cal./sq. cm./sec. or less than the heat received by convection. As a matter of fact, although the amount leaving the bottom cannot be actually determined here, it is very nearly equal to that entering the top and therefore H_1 is very small.

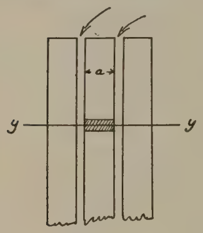

Fig. 3.

Turning to radiation in the open spaces between benches, it can be seen at once that if the vertical temperature gradient is uniform, there will be the same temperature difference between the given section and the hotter regions, and the section and the lower regions. The mean temperature of the wall above will be assumed at 2410 and below at 2390. The heat retained will then be that received minus that radiated. The Stefan-Boltzmann radiation law states that $H = K(T^4 - To^4)$,[1] or in this case:

$$H_2 = 1.36 \times 10^{-12} \times 0.20\,(1595^4 - 1589^4) - (1589^4 - 1583^4)$$
$$H_2 = .0047 \text{ cal./sq. cm./sec.}$$

This is about the same amount received by convection. On the other hand the heat transfer by radiation between the charge and crown or charge and flue bottoms may be very large. If the crown is 2600° and the top of the charge 2500°,

$$H_2 = 1.36 \times 10^{-12} \times 0.2\,(1701^4 - 1645^4) = .28 \text{ gm. cal./sq. cm./sec.}$$

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[1] In this equation $K = 1.36 \times 10^{-12}$ for the units used here, but the emission of coefficient must also be put in. This value is not well known at high temperatures but 0.20 seems to be the most conservative.

If the bottom of the charge is 2300° and the flue bottom is 1800°,

$$H_2 = 1.36 \times 10^{-12} \times 0.2\ (1533^4 - 1256^4) = .83$$

This indicates at once the great importance of radiation in heating the top of the charge and cooling the bottom.

The same analysis on heat transfer will apply in a lateral direction. The heat transfer along the kiln would not be appreciable by conduction. The carrying of heat across the openings by radiation will be small as the temperature difference is small. Suppose there are twenty openings in the length of the kiln and an overall temperature difference of 50°. The temperature drop across each opening (assuming $^1/_2$ drop in benches) would be only 1.2°F.

This illustrates the well-known fact that partitions cut down the transfer of heat by radiation. With two large parallel surfaces at a given small difference of temperature there will be heat flow by radiation of a certain amount. If a thin conducting partition is placed between the walls it will take up a mean temperature and the heat flow will be approximately halved. Two partitions will reduce it to one-third, etc. This is the reason a good insulator, composed of numerous pores transfers practically no heat by interior radiation.

Analysis of Heat Flow in the Kiln

As all three methods of heat transfer are important in one place or another, it is evident that we must consider all of them in our problem. Convection and conduction depend directly on the temperature difference between the two points considered and so can be handled directly. The assumption must be made, however, that the material constants such as conductivity, specific heat, etc., are constant for the range of temperatures encountered inside the kiln. An examination of the temperature coefficients will show that this assumption is safe.

The transfer of heat by radiation is dependent both on the temperature difference between two points and on their absolute temperature. As seen from the Stefan-Boltzmann law, the absolute value of the temperature is very important, as it enters as the fourth power, and cannot be neglected like the temperature coefficient. There are only two things that can be done with the model: either run it at a low temperature (under 400°C) and entirely eliminate radiation or make the temperature distribution in the model the same as that in the large kiln.

In applying dimensional analysis to the problem, radiation will at first be neglected and the results will apply to a low temperature condition of model and large kiln. To include radiation and make similitude exact, it is necessary to make the absolute temperature of the model the same as for the large kiln.

The quantities entering into this problem will be:

Quantity	Symbol	Dimensions
Time	t	T
Length	l	L
Gas velocity	v	LT^{-1}
Gas conductivity	K_1	$HT^{-1}L^{-1}\Theta^{-1} = MT^{-2}L\Theta^{-1}$
Solid conductivity	K_2	$HT^{-1}L^{-1}\Theta^{-1} = MT^{-2}L\Theta^{-1}$
Sp. heat of gas/unit vol.	C_1	$HL^{-3}\Theta^{-1} = ML^{-1}T^{-1}\Theta^{-1}$
Sp. heat of solid/unit vol.	C_2	$HL^{-3}\Theta^{-1} = ML^{-1}T^{-1}\Theta^{-1}$
Viscosity of gas	μ	$ML^{-1}T^{-1}$
Density of gas	ρ	ML^{-3}
Kinematic viscosity of gas	ν	$L^2T^{-1} = \frac{\mu}{\rho}$
Temperature difference	Θ	Θ
Rate of heat transfer	h	$HT^{-1} = ML^2T^{-2}$
Heat quantity	H	$H = M^2T^{-1}$

Proceeding as before:

$$\begin{aligned}
h &= V^a l^b \Theta^c C_2^d \text{ or } ML^2T^{-2} = L^aT^{-a}, L^b, \Theta^c, M^dL^{-d}T^{-d}\Theta^{-d}\\
t &= V^a l^b \Theta^c C_2^d \text{ or } T = L^aT^{-a}, L^b, \Theta^c, M^dL^{-d}T^{-d}\Theta^{-d}\\
K_1 &= V^a l^b \Theta^c C_2^d \text{ or } MT^{-2}L\Theta^{-1} = L^aT^{-a}, L^b, \Theta^c, M^dL^{-d}T^{-d}\Theta^{-d}\\
K_2 &= V^a l^b \Theta^c C_2^d \text{ or } MT^{-2}L\Theta^{-1} = L^aT^{-a}, L^b, \Theta^c, M^dL^{-d}T^{-d}\Theta^{-d}\\
C_1 &= V^a l^b \Theta^c C_2^d \text{ or } ML^{-1}T^{-1}\Theta^{-1} = L^aT^{-a}, L^b, \Theta^c, M^dL^{-d}T^{-d}\Theta^{-d}\\
\nu &= V^a l^b \Theta^c C_2^d \text{ or } L^2T^{-1} = L^aT^{-a}, L^b, \Theta^c, M^dL^{-d}, T^{-d}\Theta^{-d}\\
H &= V^a l^b \Theta^c C_2^d \text{ or } ML^2T^{-1} = L^aT^{-a}, L^b, \Theta^c, M^dL^{-d}T^{-d}\Theta^{-d}\\
\rho &= V^a l^b \Theta^c C_2^d \text{ or } ML^{-3} = L^aT^{-a}, L^b, \Theta^c, M^dL^{-d}T^{-d}\Theta^{-d}
\end{aligned}$$

The equations give the following eight dimensionless constants:

$$\left[\frac{tv}{l}\right]\left[\frac{K_1}{vlc_2}\right]\left[\frac{K_2}{vlc_2}\right]\left[\frac{C_1}{C_2}\right]\left[\frac{\nu}{vl}\right]\left[\frac{h}{vl^2\Theta C_2}\right]\left[\frac{H}{L^3\Theta C_2}\right]\left[\frac{\rho vl}{\Theta C_2}\right]$$

Any one of them may be selected as a definite function and the rest grouped together as an unknown function thus:

$$h = vl^2\Theta C_2\cdot\phi\left\{\left[\frac{tV}{l}\right]\left[\frac{Kl}{vlc_2}\right]\left[\frac{K}{vlc_2}\right]\left[\frac{C_1}{C_2}\right]\left[\frac{\nu}{vl}\right]\left[\frac{H}{L^3\Theta C_2}\right]\left[\frac{\rho vl}{\Theta C_2}\right]\right\}$$

where ϕ is an unknown function which can only be determined by experiment.

The equation means that the rate of heat transfer is proportional to the gas velocity, the area, the temperature difference and the specific heat in any size of geometrically similar kiln provided all of the dimensionless products are invariable. That is, if the model is $^1/_5$ size, and the temperatures and materials are the same; v must be five times greater; t, $^1/_{25}$ as large; and H, $^1/_{125}$ as large.

If it is desired to take account of radiation the last equation becomes:

$$h = vl^2\Theta C_2\cdot\phi\left\{\left[\frac{tv}{l}\right]\left[\frac{Kl}{vlc_2}\right]\left[\frac{K_2}{vlc_2}\right]\left[\frac{C_1}{C_2}\right]\left[\frac{\nu}{vl}\right]\left[\frac{H}{L^3\Theta C_2}\right]\left[\frac{vl}{\Theta C_2}\right](\Delta)\right\}$$

where Δ is the absolute temperature.[1]

Attention should be called to the important fact that this problem is one of the few cases where exact similarity holds for changes in scale. For example, should l have occurred in two of the dimensionless products as (ν/vl) and $(\nu t/l)$ where ν is an invariable property of the medium, the scale could not be changed and still keep similarity. This difficulty arises in testing propellers and ship models and must be taken care of by experimentally determined correction factors.

Kiln	Full scale	Similar model		Wooden model	
	Value	Value	Ratio	Value	Ratio
Size—1	1	0.2	0.20	0.20	0.20
Temp. dif.—Av. inside and air	2400°F	2400	1	240	.10
Pressure differences	1	25	25	1.2	1.2
v—heated gas—ft./min.	1	5	5	.51	.51
v—equiv. air at 60°F	0.164	.83	5	.39	2.3
ν	.021	.021	1	.0022	.105
ρ	22×10^{-5}	22×10^{-5}	1	93×10^{-5}	
t	1	0.040	.040	.39	.39
K_1	.0095	.0095	1	.014	1.45
K_2	.0040	.0040	1	.00038	0.095
C_1	.000066	.000066	1	.00021	3.1
C_2	.50	.50	1	.142	.28
H	1	.0080	.0080	.00023	.00023
Vol. of heated gases cu. ft./min.	1	.20	0.2	.020	.020
Vol. of equiv. air at 60°F cu. ft./min.	.16	.031	.2	.015	.107
(ν/vl)	.028	.028	1	.028	1
(K_1/vlc_2)	.020	.020	1	.097	.62
(K_2/vlc_2)	.0080	.0080	1	.0027	4.1
(c_1/c_2)	.000132	.000132	1	.000148	1.12
(tv/l)	1	1	1	1	1
$(H/L^3\,\Theta C_2)$	1	1	1	1	1
$(\rho vl/\Theta C_2)$	1.83×10^{-7}	1.83×10^{-7}	1	27.3×10^{-5}	1490
Calories needed to heat charge (C_2L^3)	1	.0080	.0080	.0022	.0022
Calories lost through wall (K_2l^2t/l)	1	.0090	.0080	.0080	.0080
Calories lost in flue gases (vtl^2)	1	.0080	.0080	.0080	.0080
Efficiency	1	1	1	.11	.11

---

[1] Δ is not dimensionless as are the other products, but it is put in here to show that it must be the same for model and full scale.

It might be reasonably concluded, in analogy with the equation of fluid resistance, that some of the dimensionless products could be omitted as unimportant. Careful experiments will show which ones, if any, can be neglected, but at present we have insufficient data to decide. At any rate, as it is possible to keep all the products constant, it certainly is the safe thing to do.

As a concrete example, there is tabulated the computed characteristics of a $^1/_5$ scale model of a kiln, geometrically similar, of the same materials and run at the same temperature as the large structure. There is also shown the characteristics of a similar model, but constructed of white-wood and run at $^1/_{10}$ of the full scale temperature. If the models are run under these conditions similitude will be attained.

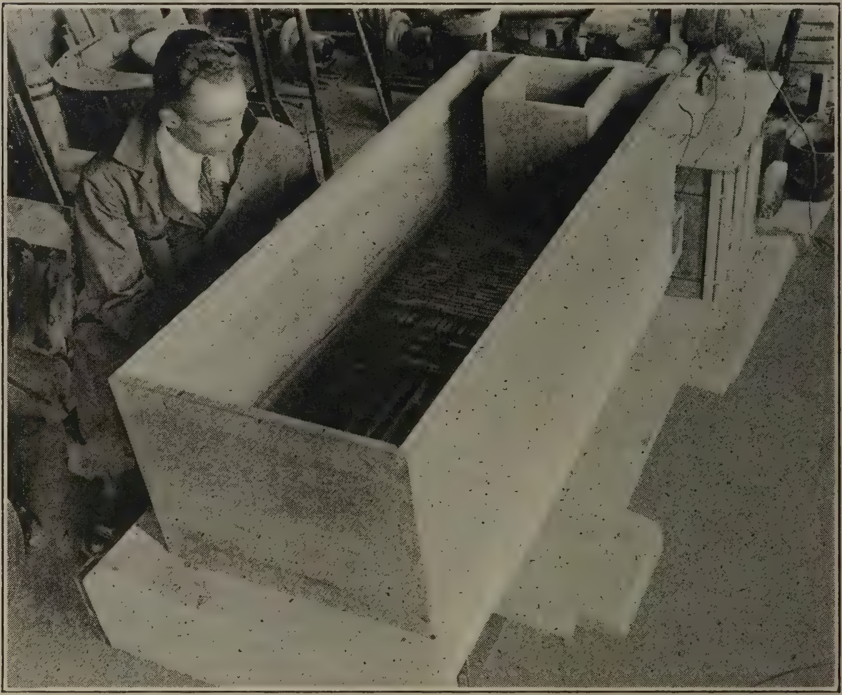

FIG. 4.

The preceding table brings out clearly the characteristics of the model. There is, however, one feature that looks at first glance incompatible; the temperatures at all points in the model are supposed to be equal to that of a similar point on the large kiln, but the wall of the model is comparatively thin and therefore a higher outside temperature would be expected. This can be explained by considering that the gases in the model are moving very rapidly and are bringing heat to the walls rapidly. To obtain similarity, therefore, the heat should be carried away from the outside equally rapidly, that is, the air around the kiln should be circulated more rapidly to correspond with the action inside the kiln. This velocity on the outside should be such as to make the product (ν/vl) constant for the model and large kiln. As ν is the same in both cases, (vl) need only be considered. The air velocity around the large kiln is low and uncertain, so the corresponding value for the model cannot be obtained analytically. It is very simple, however, to hold the outside of the model to any given temperature by trial.

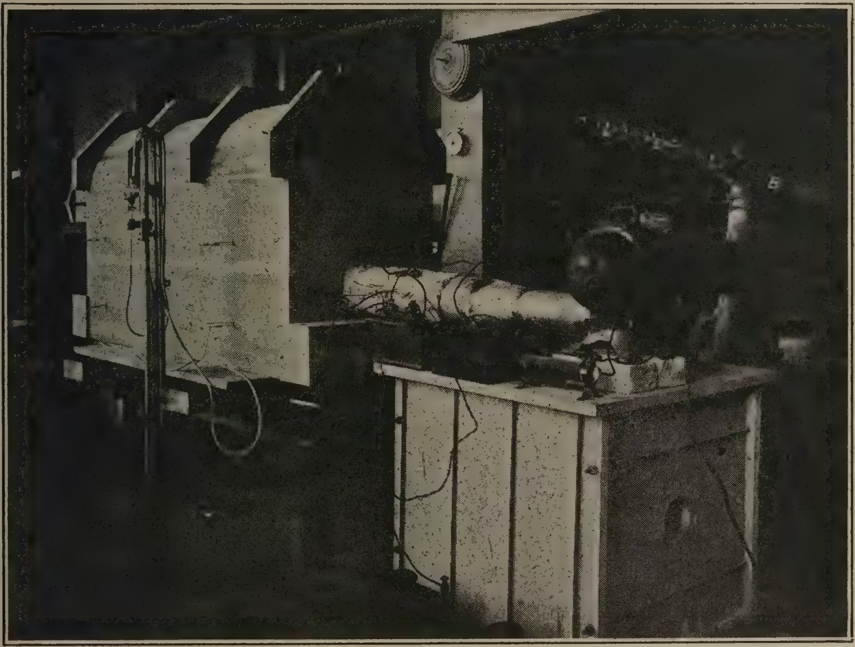

Fig. 5.

Construction of the Models

A wooden model is easily constructed and a great deal of information can be obtained from it, such as the pressures in the kiln, the path of the gases, the resistance of the passages, and to some extent, the evenness of heating. The bricks can be represented by small blocks, and the temperatures can be read by thermocouples or mercury thermometers. The highest temperature possible with a wooden model is about 350°F. Heated air can be supplied by a small blower and a grid of heating wires. Such a model is shown in Figs. 4 and 5.

The high temperature model is more difficult to construct because of the high velocity and pressures, but a great deal more can be learned from it. The walls and crown should be laid up of the same bricks as the large kiln, with joints carefully fitted. The charge can be represented by a series of perforated tiles.

Due to the large amount of combustion gases, it is sometimes necessary to burn the fuel outside of the model in a separate combustion chamber and then pass the hot gases through the burner holes. The temperatures can be measured with platinum thermocouples or optical pyrometers. The great rapidity of a burn in the model is an important advantage.

Conclusions

While no complete comparisons have as yet been made between a large kiln and its model, it is felt that model tests can predict with considerable accuracy the following characteristics of a kiln:

1. The pressures and velocities throughout the kiln and flues.
2. The distribution of temperature throughout the kiln at any stage of the burn.
3. The heat lost in the stack.
4. The heat lost through the walls.
5. The amount of fuel required to burn to a given temperature.
6. The time required to reach a given temperature.

On the other hand, the model has the disadvantage of not being able to reproduce the burner flame to scale, so that a model would not be suitable for trying out burners.

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1.—Bridgman, "Dimensional Analysis."

2.—McAdams and Frost, "Heat Transfer for Water Flowing Inside Pipes."

3.—Walker, Lewis and McAdams, "Principles of Chemical Engineering."

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ORIGINAL PAPERS

COLLOIDS IN GLASS[1]

By Alexander Silverman

ABSTRACT

A discussion of the various elements and compounds found in a colloidal state in glass. Attention is called to the similarity of colloidal behavior in vitreous and aqueous media. Theories and experimental evidence are furnished to account for the formation and destruction of the colloidal state.

Introduction

Glass has been defined as a liquid mixture, or mutual solution of silicates (alone or with borates and other salts), whose viscosity is so high as to make it appear solid (solid solution) at ordinarily prevailing temperatures.

Solutions of silicate-soluble salts in glass resemble those of other combinations soluble in water,[2] in numerous instances. Auric compounds yield a yellow solution; cupric, blue; uranium, yellow by transmitted and fluorescent green by reflected light; the blue color produced by cobalt is like that obtained in strongly acid aqueous media; ferrous, green; ferric, yellow; manganous, colorless, as in dilute aqueous solution, and blue-green, rose or amethyst on oxidation; polysulphides, yellow to amber;

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[1] Advance chapter from "Colloid Chemistry—Theoretical and Applied," preprinted with the permission of Jerome Alexander, Editor of the volume, but not available for reprinting in other publications.

[2] A. Silverman, "Similarity of Vitreous and Aqueous Solution," *Jour. Ind. Eng. Chem.*, 9, 33 (1917).

chromium, green and yellow. Salts which are colorless in aqueous solution are also colorless in glass, if in the same state of oxidation.

Then we have the colloidal suspensions like the red, purple, blue and various colors produced by gold and other metals; opalescence by aluminium-bearing substances, stannic oxide, titanic oxide, phosphates, etc. Presence of strong electrolytes interferes here as in water solutions.[1]

Foundations for Claim of Existence of Colloidal Suspensions in Glass

I. An example more frequently cited than any other, concerns the use of gold compounds. When gold was first used to color glass, it was introduced in colloidal form in purple of Cassius (Kunkel 1630–1703). Of course, this material dissolved in the melt, and today gold chloride is sprinkled on part of the batch (mixture of raw materials) and answers the same purpose.

When gold-bearing glass, of fairly high concentration, is drawn from the pot it is yellow. Although some claim that this color is due to submicrons, the author feels that the gold is in true solution as an auric compound, since all gold-glass batches contain oxidizing agents.

Bancroft states that colorless glass will result through chilling under either oxidizing or reducing conditions and that consequently the gold might be in true solution or so peptized by the glass that the colloidal particles are too small to have an effect on the beam of light.[2] The fact that a ruby glass may be produced by exposing the yellow or colorless glass to radium emanation seems to further substantiate the true-solution claim.[3] Reheating the yellow glass (colorless in more dilute or thin sections) in a reducing flame, first produces a pink color. Repeated, more prolonged or more intense heating will yield pink, red, purple, blue. After sufficient treatment, the glass looks brown, or livery, by reflected light and blue by transmitted, like a gold chloride solution in water, boiled with oxalic acid crystals, where the precipitate is brown and the supernatant liquid blue. The colors, in earlier stages of reduction, correspond to the succession observed when an aqueous solution of gold salt is reduced by phosphorus dissolved in ether, but glass offers the advantage that the colloidal particles in the solid solution are not free to move about as they do in water and so can be observed more easily under the ultramicroscope. As the gold content in all of the glasses differed, the estimation of the size of particle was apparently not dependent on the quantity of metal present. That the size of colloidal gold particles of various colors in glass corresponds fairly well with their dimensions in aqueous media is also shown by Zsigmondy.[1]

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[1] W. J. Sutton and A. Silverman, "The Electrical Conductivity of Sodium Chloride in Molten Glass," *Jour. Amer. Ceram. Soc.*, **7** [2], 86 (1924).

[2] W. D. Bancroft, "Applied Colloid Chemistry," 306 (1920).

[3] J. C. M. Garnett, "Colours in Metal Glasses, in Metallic Films, and in Metallic Solutions—II," *Phil. Trans.*, **205A**, 251 (1905).

Some of Zsigmondy's data follow:

SIZE OF GOLD PARTICLES IN GLASS[2]

					Size of particle in $\mu\mu$	
Glass	Color by transmitted light	Color of particles	Cu. mm. gold per cu. dm. glass	Colorimetric estimation	Based on total gold content	Based on colorimetric determination
H	Pink	Light green	..	1.0	....	3.9– 6.9
F	Light red	Light green	8.0	4.4	9.3– 12.5	7.6–10.2
Cc	Red	Green	13.3	1.34	20.6– 32.8	9.6–15.3
Db	Blue to violet	Brass yellow	6.8	..	68 – 74	....
Da	Blue	Copper red	6.8	..	68.8–103	....
D	Livery	Deep yellow	10.1	..	131 –173	....
A	Colorless	Golden yellow	12.6	..	487 –791	....

In this same publication experiments are described showing the effect of heat on color. A colorless strip of gold glass, which had been cooled very slowly, was reheated until it began to melt at one end, while the other end still remained cool. On cooling, the heated end was deep red and the color gradually diminished to colorless at the other end. Another piece of poorly prepared glass showed blue at the reheated end, shading through violet and red to colorless at the cold end. The poorly made specimen probably had more heat treatment in manufacture and before tests were made on the strip. Hence, larger colloidal particles formed, which colored the glass blue by transmitted light.

Zsigmondy further points out that the "working temperature of colorless molten gold ruby glass is several hundred degrees lower than the temperature at which it is melted," and that while most of the gold is in true solution, submicroscopic nuclei probably exist which serve as centers for further growth. He also calls attention to greater crystalloid solubility at 1350–1400°C which accounts for the disappearance of color and return to true solution. That color production is in part dependent on cooling rate can be seen in pressed discs which are frequently lighter at the edges than in the center, due to variable conductance of the iron mold. It is claimed that color is not only dependent on the size of the particles, but on their shape as well.[3]

One-tenth of one per cent of gold or less will color glass, the facility of color production depending on the composition of the glass. Lead, tin and barium-bearing glasses require less gold than lime-glass. It is said that increasing stannic oxide enhances uniformity of red color and minimizes blue formation.[1]

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[1] R. Zsigmondy, "Colloids and the Ultramicroscope," 132 (1909).

[2] H. Siedentopf and R. Zsigmondy, "Uber sichtbarmachung und grössenbestimmung Ultramikroskopischer Teilchen mit Besonderer Anwendung auf Goldrubingläser," *Annal. d. Phys.*, **10** [4], 10 (1903).

[3] G. Mie, "Die Optische Eigenschaften Kolloidaler Goldlösungen," *Phys. Zeit.*, **8**, 769 (1907); J. C. M. Garnett, "Colours in Metal Glasses, in Metallic Films, and in Metallic Solutions—II," *Phil. Trans.*, **205**, 241 (1906).

And now a bit of comment on the author's personal experiences. A gold ruby lead-glass was reproduced repeatedly for commercial use in fairly large-sized melts with good results. The color was uniform. In some small scale investigations as to the possibility of changing the color intensity, melts were made in covered Battersea crucibles. Their contents were poured into iron molds, forming flat buttons. These buttons were placed on asbestos board in an electric muffle furnace and heated up slowly until the glass melted, when the current was shut off and the furnace allowed to cool very slowly to room temperature. A set of buttons from a single crucible all showed nearly every color of the rainbow. Nor were the colors similarly located in the various discs. While these pieces constitute interesting museum specimens, the results are puzzling.

II. The controversy between advocates of the cuprous oxide and colloidal-copper theories concerning copper-red glasses eliminates them from our discussion. The matter is apparently unsettled.[2]

III. Selenium glasses appear black when drawn from the pot. On cooling, they may become colorless, slightly opalescent, yellow, orange, pale red or deeper red, depending on the alkalinity of the batch and the unvolatilized selenium remaining in the glass.

Batches for selenium glass usually contain sand, zinc oxide, alone or in partial substitution for lime (lead compounds are rarely used with the sulphur family elements); potassium carbonate, alone or partly replacing sodium carbonate; antimony trioxide or cadmium sulphide; and a reducing agent, such as carbon, flour, sugar, or sulphur. Selenium is introduced as element (black or red form), or as sodium selenite. Whether introduced as element or compound, a sufficient amount of reducing agent insures conversion to element.

When the glass is reheated, it again turns black and on cooling assumes an orange-red to a garnet shade, depending on the selenium content and heat treatment. High alkali produces a deeper shade. The deep red glasses show no colloidal particles in the ultramicroscope, so the color, especially since it is deeper with higher alkali content, is probably due to polyselenides,[1] just as the yellow or amber color with sulphur or reduced sulphates is due to sulphide or polysulphide formation. In salmon pink, opalescent and almost colorless specimens of selenium glass, colloidal particles may be seen. The reaction is represented as follows:

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[1] H. T. Bellamy, "The Development of Improved Gold Ruby Glass," *Jour. Amer. Ceram. Soc.*, **2** [4], 313 (1919).

[2] A. E. Williams, "Notes on the Development of the Ruby Color in Glass," *Trans. Amer. Ceram. Soc.*, **16**, 284 (1914); H. A. Seger, "Collected Writings," **2**, 734 (1902); G. G. Stokes, *Math. and Phys. Papers*, **4**, 245 (1904); W. Rosenhain, "Glass Manufacture," 181 (1918); P. Zulkowski, "Uber die Natur einiger Kupfergläser," *Chem. Ind.*, **20**, 134 (1897).

$$\text{“}3Na_2O + (2n + 1)Se \rightleftarrows 2Na_2Se_n + Na_2SeO_3$$

the equilibrium being shifted to the left at high temperatures and in mixtures rich in SiO_2, and to the right at lower temperatures and in mixtures richer in alkali."[2] The colloidal particles are said to be less than 40 $\mu\mu$ diameter.

While discussing the effect of selenium, it might be well to include the related elements, sulphur and tellurium. Sulphur and tellurium act as coloring agents under reducing conditions similar to those mentioned for selenium, forming polysulphides and polytellurides, which color the glass yellow and red, respectively. Considering the sulphur family, we may say that the color of the glass varies from yellow to red progressively with increasing atomic weight of the elements, alkalinity of the batch, and reducing conditions. Before reduction, or through subsequent heating, and oxidation, or with increasing acidity of the glass, or with increasing viscosity of the glass (dependent on composition) the colloid-forming tendency progresses in the sulphur family with increasing atomic weight.[3] Sulphur and tellurium glasses which display colloidal phenomena are blue.

IV. Soda glasses are colored blue to violet by X-rays and radium emanation, and potash glasses brown. The sodium color closely resembles that of blue rock salt. This color has been produced in the laboratory by exposing salt crystals to radium emanation, cathode rays or sodium vapor.[4] The coloring of quartz and gems by ultra-violet light and radium is common knowledge today.[5]

V. The dichroic effect seen in aqueous solutions of chromic salts and in the mineral Alexandrite has been obtained in glass by the writer. The color in aqueous media has been attributed to colloidal phenomena, and the color of the glass closely resembles this. If two cells containing the green chromium solution are superimposed, the transmitted light is dark red. Superimposed pieces of chrome-green glass display the same phenomenon.[1]

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[1] P. Fenaroli, "Uber das allgemeine Verhalten der Elemente Schwefel, Selen und Tellur in Natron-Kalziumsilikatgläsern mit besonderer Berücksichtigung der durch dieselben bewirkten Färbungen," *Kolloid-Z.*, **16**, 53 (1915).

[2] P. Fenaroli, "Red Pigment with Selenium Base," *Ind. Chim.*, **13**, 98 (1913); through *Chem. Abs.*, **7**, 2840 (1913).

[3] P. Fenaroli, "Das Tellur als Färbemittel in den Natronkalksilicatgläsern," *Chem.-Ztg.*, **38**, 873 (1914).

[4] H. Siedentopf, "Ultramikroskopische Untersuchungen über Steinsalzfärbungen," *Ber. deutsch. phys. Ges.*, **3**, 268 (1905).

[5] C. Doelter, "Das Radium und die Farben," (1910).

VI. Platinum and other chemically inactive metals may color glass. The author has found that platinum electrodes, in molten soda-lime glass subjected to an electric current, will discolor the glass near the electrodes if the current frequency is not sufficiently high. While these glasses have not been examined ultramicroscopically, the author feels that the platinum is in colloidal suspension, as the conductivity cell was filled with broken glass towards which platinum should prove inert after the glass had melted.

VII. Opalescence is considered a colloidal phenomenon. This is produced in glasses through the introduction of arsenious oxide, stannic oxide, calcium phosphate, cryolite, or mixtures of aluminium and fluorine-bearing compounds. The author's researches in this field have been confined largely to alumina-bearing glasses and it has been interesting to observe the effects of various agencies on the colloid. It was found that fused electrolytes, like NaCl and Na_2SO_4 dissolved in opal glasses, destroyed opalescence, just as dissolved salts would destroy it in aqueous media, and produced alabaster glasses in which opalescence was no longer perceptible, the glasses transmitting white light instead of fiery light.[2]

In alabaster glasses, the suspended particles are larger than in opal glasses, in fact so much larger that the phenomenon of opalescence disappears and white light is transmitted. Opal glasses behave like colored glasses which owe their color to the size of the suspended particles. If a light opal glass is reheated and cooled, the color intensity increases. The amount, degree and length of reheating determines the color and size of particles. As is the case with metal-colloid colors, true solution is effected if the glass is subjected to prolonged heating above its melting point. Even alabaster glasses may lose their color or become opalescent under these conditions.

Alumina in aqueous suspension is regarded as a positive colloid. That the ions in a silicate or borosilicate glass, devoid of chlorides or sulphates, should not destroy opalescence is accounted for by the fact that electrical conductivity in a solid glass is due to positive metal ions which convey a direct current according to Faraday's law.[3] Heating solid glasses which have been subjected to a direct current, results in the evolution of a quantity of oxygen, through breaking down of the silicate ions, equivalent to the metal liberated. Here the positive ions carry all the current while the negative silicate ions form a mechanically rigid framework.[1] That NaCl dissolved in molten soda-lime glass, ionizes and increases the electrical conductivity, has been shown through recently conducted researches in the author's laboratory.[2] In these investigations .95% and 1.41%, respectively, of sodium chloride were added to the glass and the conductivity studied above 750°C. While the conductivity does not correspond to that of an equal concentration in water, results compared with those obtained for the conductivity of fused mixed salts[3] indicate ionization of the NaCl in molten soda-lime glass. The author concludes, therefore, that opalescence in alumina-bearing glasses free from dissolved chlorides or sulphates is due to a positive colloid unaffected by the positive sodium and other metal ions present. Further that when alkali chlorides or sulphates are added, the negative chloride or sulphate ions cause precipitation and an alabaster glass results.

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[1] A. Silverman, "Similarity of Vitreous and Aqueous Solution," *loc. cit.*

[2] A. Silverman, "Alabaster Glass: History and Composition," *Jour. Amer. Ceram. Soc.*, **1,** 247 (1918).

[3] M. LeBlanc and F. Kershbaum, "Elektrizitätsleitung durch Glas," *Z. phys. Chem.*, **72,** 468 (1910).

An investigation of the history of clouded glasses indicates that as far back as the seventeenth century, or possibly earlier, and until the manufacture of salt-free and sulphate-free alkali carbonates was perfected, all clouded glasses were alabaster and displayed little or no opalescence.[4] Natural and LeBlanc alkali carbonates contained sulphates and chlorides, and prevented opalescence, but with the introduction of pure potassium carbonate from Stassfurt and sodium carbonate made by the Solvay process, opal glasses came into being. It is interesting to note that with the advent of opal glasses, the art of making alabaster glass was lost for the time being, and that when the author began his work in the glass field in 1902, the production of this type of glass was his first problem.[5] The effect was produced by adding salt to an opal batch, and later with salt cake and other sulphates and chlorides. Leave these out of the batch and the glasses are opalescent.

Next, another observation must be recorded which is of interest. The alabaster effect failed to materialize unless an oxidizing agent was present in the batch. In other words, a batch containing salt yielded no opacity in the glass unless a nitrate was employed. When sulphates were used instead of chlorides, their partial decomposition yielded the necessary oxygen. Nitrates without chlorides insured opalescence but failed to produce the alabaster effect. It was also found that opal or alabaster glasses which had become transparent through prolonged heating above the melting point, would regain their color if air was blown through the molten glass which was next allowed to cool. What does this mean? Is it an argument against the theory that opalescence in glass is due to colloidal suspensions and that these are precipitated or congealed into larger particles through the influence of chlorides or sulphates? The author thinks not. The high temperature of molten glass, if this is heated too long, may result in the formation of aluminites, aluminates, or aluminium silicates or borates, which enter true solution and yield a clear glass. Oxidizing agents and air probably cause a transformation in these compounds with the formation of colloidal Al_2O_3. The ionized chlorides or sulphates then precipitate the alumina.

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[1] C. Tubandt, "Uber Elektrizitätsleitung in festen Kristallisierten Verbindungen," *Z. anorg. allgem. Chem.*, **115,** 105 (1921).

[2] W. J. Sutton and A. Silverman, *loc. cit.*

[3] H. M. Goodwin and R. D. Mailey, "On the Density, Electrical Conductivity, and Viscosity of Fused Salts and Their Mixtures," *Phys. Rev.*, **25,** 469 (1907); **26,** 28 (1908); C. Sandonnini, "Electrical Conductivity of Mixtures of Fused Salts," *Atti acad. Lincei*, **24** [I], 616 (1915).

[4] A. Silverman, "Alabaster Glass: History and Composition," *loc. cit.*

[5] A. Silverman, "The Chemist and the Glass Manufacturer," *Trans. Amer. Ceram. Soc.*, **12,** 186 (1910).

VIII. Colloids in enamels and other decorative materials have not been discussed as the author feels that this topic could best be developed by a specialist in enamels. Reference should, however, be made to mirrors, in which the silver film, deposited on glass from ammoniacal silver nitrate by formaldehyde[1] and other reducing agents is of colloidal thickness as it appears blue by transmitted light.

If reference to colloidal effects in glass by substances other than those mentioned in the chapter has been omitted, this has been done because the information appearing in technical publications is controversial or insufficiently established.

It can be said, in conclusion, that glass may contain elements and compounds in colloidal suspension and that, except for freedom of motion, colloids in glass are similar to those in liquid media and subject to the same laws.

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University of Pittsburgh

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[1] A. Silverman and P. D. Neckerman, "The Silvering of Glass," *Trans. Amer. Ceram. Soc.*, **17**, 505 (1915); A. Silverman and R. M. Howe, "The Deposition of Silver Films on Glass," *Jour. Ind. Eng. Chem.*, **9**, 1032 (1917).

THERMAL EXPANSION OF FUSED QUARTZ[1]

BY GEORGE E. MERRITT

The thermal expansivity of fused quartz does not seem at first thought particularly pertinent to the glass industry. Fused quartz is, however, the one constituent of glass which is indispensable. I take it that a glass which did not contain silica would be a sort of freak, and I hope to show that there is a little closer relationship between fused quartz and other glasses than you perhaps realize.

Fused quartz really is a glass; not a mineral. It differs very largely from crystalline quartz in its ordinary as well as its special forms and from any crystalline form of quartz. It is neither alpha quartz nor beta quartz, neither crystobalite nor tridymite. Each of these has a characteristic thermal expansion curve, but none of them have expansivities different from those of ordinary glass.

Fused quartz is remarkable among solids because of the smallness of its coefficient of expansion throughout the whole temperature range investigated. We, at the Bureau of Standards, have carried these determinations higher than anyone else, as far as I know, that is to 1200°C (about 2200°F). Carl Scheel, a German physicist, has determined its expansivity down to −200°C.

A comparison of the coefficients of some ordinary materials will be of interest:

	μ/meter per degree C	Temp. range, degree C
Ordinary steel	12	20 to 500
Electric light bulb glass	9	20 to 400
Pyrex glass	4	20 to 500
Fused quartz	0.5	20 to 1000

Near −70°C a sample of fused quartz reaches a minimum in length then, with further decrease in temperature, it expands. This expansion continues as the temperature is lowered to −200°C. Above −70°C the sample expands: the expansivity increases gradually until at room temperature it has the value .5 μ per meter per degree C which it maintains almost unchanged to 1000°C. The expansion curve between room temperature and 1000° is slightly convex upward, but so nearly straight that only the most exact measurements show any curvature whatever.

At about 1000°C the expansivity increases, reaching a maximum at about 1100° of about 1.2 μ per meter per degree before softening commences. At 1140° the sample becomes soft enough to sink slightly under a few grams weight.

If held at a temperature above 1020°C, fused quartz will continue to expand at constant temperature. In the only determination made, this growth was found to have produced no permanent change in the size of the specimen. It is suspected that the cooling schedules were the determining factors in the case.

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[1] Presented at the Atlantic City Meeting, Feb., 1924 (Glass Division).

The similarity in shape between the thermal expansion curves of fused quartz and those of several kinds of glass is shown in Fig. 1.

CHAIRMAN: In speaking of fused quartz as a perfect glass I am sure all of us dream of the time when we can make packers' jars and everything else out of pure silica and make it in a tank. Dr. Merritt, can you give us a value for the average coefficient of expansion of quartz between 0 and 900? It seems to be almost a straight line.

BUREAU OF STANDARDS
WASHINGTON, D. C.

DR. MERRITT: .5 of a micron per meter per degree. Some investigators in Europe have found values as high as .56 and others as low as .48. I consider this difference largely due not to experimental error but to the difference in the fused quartz. Fused quartz is not absolutely pure except under very exceptional conditions and .5, I think, is as close as we can speak of a thermal expansion coefficient for fused quartz in general.

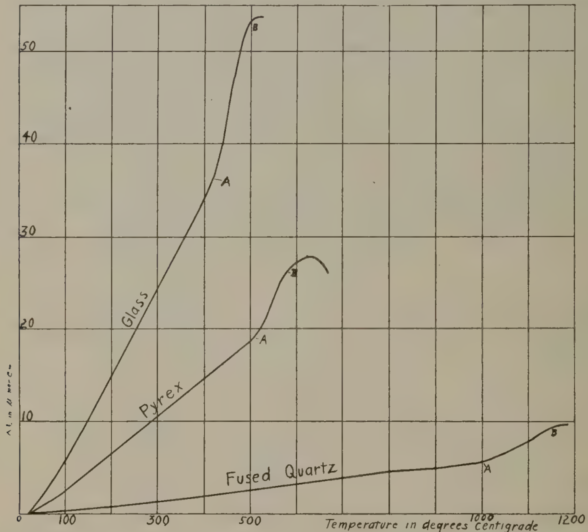

FIG. 1.—This figure shows the relative expansions of glass, pyrex and fused quartz plotted on the same scale. The similarity of the shapes of the curves is apparent.

DR. WASHBURN: A liquid such as fused quartz which shows a minimum in its expansion curve is similar in that respect to water. Such liquids belong to a class known as associated liquids. If such an association exists with a high viscosity we have there an equilibrium which will not respond readily to changes in temperature. In other words, although the quartz might be chemically pure SiO_2 two different samples of fused quartz might still show different coefficients of expansion. Was more than one sample of fused quartz from different sources and perhaps with different heat treatments studied? A second question is with reference to the behavior of the fused quartz after it is held at temperatures around 1200°. We know that under those conditions there is a slow transformation into cristobalite. Has any investigation been made of these samples and is there any evidence that such transformation occurred to an appreciable extent?

Dr. Merritt: To answer the first question: The expansivities of about 8 samples from different sources were measured and found to be sufficiently different so that we could detect a difference. This sample from which I took that curve (Fig. 1) that I put on the slide with the two glasses was measured three times, and the first time when it was badly strained it was quite a bit different from the other two. The second two curves fell almost on top of each other and with very slight differences except in the uppermost part of the curve. The first two times I did not carry it quite as far as I did the third time because I would not be able to run it again after carrying it to 1198°. I was not at all sure that there would be any surface left at all but there was enough surface left so that I could follow the curve back down for a considerable portion of the way, in fact, until as far as I had patience to carry it. It came down parallel with itself just as the regular glass curves do. I notice that you refer to fused quartz as a liquid. I am not at all sure what it is but I belong to the school which considers glass as a highly viscous liquid. I know there are some here who would differ with that and I would not be at all dogmatic on that point.

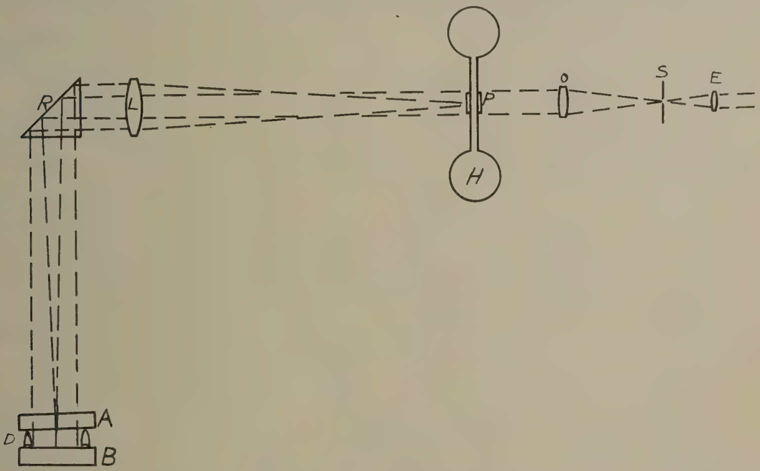

Fig. 2.—This figure is a diagram of the optical parts of the apparatus used in measuring these thermal expansions.

The second question has reference to formation of cristobalite. I did not hold that specimen at 1200° any longer than I could possibly help both because I wanted to be able to follow it down and also because I did not want to ruin my furnace any more than I had to, and so there was no evidence of any formation of cristobalite or tridymite during the time that I held it.

Dr. Washburn: Did you examine it optically afterward?

Dr. Merritt: No, I did not examine it optically except as to its clearness. It was perfectly clear, and the plate showed, when examined separately, no disturbance of the fringes. I did that so as to be able to examine the surfaces and the changes of parallelism, if any. I did not turn them over to Dr. Insley to look for cristobalite because I did not think it had been there long enough.—Perhaps 20 minutes above 1150° would be the extent of the heating.

Chairman: I asked Dr. Merritt to give this paper, knowing that you were interested in fused quartz and also in the apparatus which he used. There are several ways in which expansions are measured but I have no doubt that this is the most accurate method. How long does it take to prepare a sample of glass for this work?

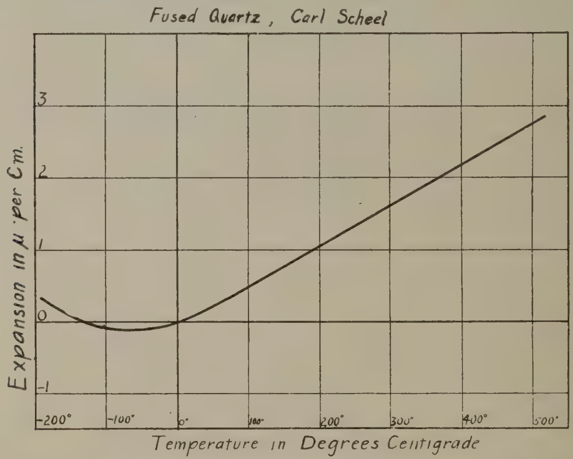

Fig. 3.—This curve, drawn from data obtained by Scheel shows the behavior of fused quartz below room temperature. Data obtained at the Bureau of Standards to −50 °C confirm this curve.

Dr. Merritt: It depends altogether on whether it is desired to have a record of the homogeneity of the specimen. If it is wished to measure three samples from the glass from different parts of the melt, so that the difference in thermal expansivity of the three parts can be measured at the same time as the average thermal expansivity of the whole thing, it takes a little longer. When only an average coefficient is desired it takes only about 15 or 20 minutes to get the specimen into shape, if you have luck, and perhaps an hour or an hour and a half if you have bad luck.

Chairman: How long does it take to make the run after you have prepared your sample?

Dr. Merritt: We generally run the specimen up at 3° to $3^1/_2$° a minute and you can figure out for yourself as to the amount of time it will take when you know how high you want to carry your run. If it is only to 500°, and most glass cannot be carried much higher than that, it will not take very long.

Chairman: It is almost straight up to the critical point but can you carry it up to 100° in a couple of hours or less?

Dr. Merritt: Yes, if you carry it up to 100°. To prepare the specimen perhaps you could do it in an hour or two.

Chairman: You have only done one sample a day because you had to let your furnace cool down?

Dr. Merritt: If you had several furnaces one man could run two samples a day or maybe more. I think though, that it would be very rash business to try to judge a glass from its thermal expansivity of 100° because although the glasses may have very similar expansivity the upper part of the thermal expansion curve gives you so much information about the annealing point and all that sort of thing, that as long as you have the specimen in the furnace you might as well run it up a few points higher. As a matter of factory control where the determinations are all in glasses of similar type, a run to 100° would be enough to detect change.

Dr. Silverman: In connection with our work on electrical conductivity, we found an article by Foussereau, who shows that a glass conducts better when tempered than when annealed and that in certain lime glasses this conductivity decreases two or three times on reheating and annealing. Consequently I am wondering what the conditions are in the fused quartz. Dr. Washburn referred to this in part. I am wondering whether any of these specimens were treated and annealed, or studied under special conditions of that sort.

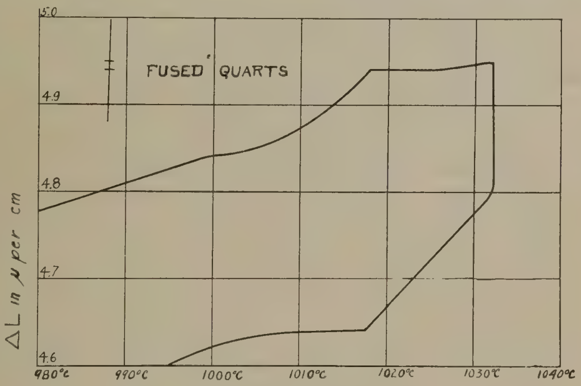

Fig. 4.—When held at any temperature above 1020°C fused quartz increases in size at constant temperature, but returns to its original length when cooled. This curve represents the behavior of a sample of fused quartz held for 30 minutes at 1032°C.

Dr. Merritt: The expansivity, of course, is different; that is, the shape of the curve is quite different. I am sorry I did not have prepared a comparison of two curves of annealed and unannealed quartz, that is, on the first and second runs on this sample you see very easily the difference there; as to the other matter of strain or change in index of refraction or anything of that sort I could not say at all.

Dr. Silverman: In what direction does the change take place? Is the expansion of an annealed specimen greater than that of a chilled specimen?

Dr. Merritt: In the first part of the curve the expansion of the chilled specimen is a little less than that of the expansion of the annealed specimen, but it is very little less. If it were drawn on the same scale which I showed you there in which the glass was almost a straight up and down curve you would not be able to see any difference between the two curves at all but when drawn on a large scale it shows a little difference at the point where the annealing takes place between 1000° and 1100°C. The chilled quartz flattens off just as glass does; it becomes almost level, almost zero expansion, for a little way (showing the release of the strain) and at the point where expansivity increases it is likely to expand more than the fused quartz which has been already annealed.

CHAIRMAN: Did you prepare specifications for this apparatus so that anybody who wanted one could order it?

MR. MERRITT: I have not done that. I prepared several slides which give the picture of the apparatus, a diagram of the optical parts of the apparatus which could be made and I could tell anyone where the optical parts could be obtained, whether they could be readily made or whether you could make them yourself.

AN ADIABATIC METHOD FOR STUDYING SPONTANEOUS HEATING OF COAL[1]

By J. D. Davis[2] and J. F. Byrne[3]

ABSTRACT

An adiabatic calorimeter is described, by means of which the spontaneous heating characteristics of dry pulverized coal can be studied, so as to obtain a direct measure of the rate of spontaneous heating at different temperatures, uninfluenced by various heat interchange factors. Specimen time-temperature curves of different coals are presented, which show approximately the same rate of heating over corresponding temperature ranges. From these curves, it is concluded that the main characteristic of spontaneous heating is that the rate of heating is an increasing function of the temperature. An empirical formula is developed, $\Theta = K \frac{(a + T)}{(b-T)}$ for which the constants, K, a and b, are determined for a Pittsburgh coal; Θ = temperature, and T = time. From this formula, it is concluded: (1) no heating will take place below 26.27°C; (2) the time required for Pittsburgh coal to heat from this temperature to ignition is 144 hours, both the coal and the oxygen used being moisture free.

Introduction

A study of the spontaneous heating of coal is of practical utility, primarily because of its bearing on the problem of coal storage. The question of why coal heats spontaneously is not of such vital importance in this connection as a clear understanding of the conditions under which it will heat. Experience in the storage of coal[4] points strongly to the conclusion that while all known coals have been stored without spontaneous heating, there are conditions under which practically all bituminous coals have heated in storage. It is clear therefore that in order to successfully cope with the problem, the physical conditions more particularly which influence spontaneous heating reactions must be known. The nature of the chemical constituents of coal which enter into the reactions and their quantitative effect is of secondary importance. This viewpoint led the writers to adopt a physical method of investigation rather than one based mainly on chemical procedure. In a word, the idea was to induce artificially and control spontaneous heating of a sample of coal so that all factors affecting its rise in temperature could be eliminated except the one due to oxidation. Once having realized this condition practically, other conditions—variable factors contributing to the spontaneous heating of coal, such as air supply and moisture content—could be introduced and their effects estimated. Thus if no heat exchange is permitted (the adiabatic condition) between a specimen of coal under investigation and its surroundings, any rise in

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[1] Published by permission of the Director, Bureau of Mines. Recd. July 11, 1924.

[2] Fuels Chemist, Pittsburgh Experiment Station.

[3] Junior Chemist, Pittsburgh Experiment Station.

[4] H. H. Stoek, C. W. Hippard, and W. D. Langtry, "Bituminous Coal Storage Practice," Illinois Eng. Exp. Station, *Bull.* **116,** p. 23, 1920, 149 pp.

temperature of the coal must be due to heat generated therein—that is, to spontaneous heating.

The purpose of this paper is to describe apparatus developed in the Bureau of Mines laboratory for the investigation of spontaneous heating of coal with adiabatic control, and to show briefly the extent of heating which takes place when the adiabatic condition is maintained.

The Problem of Adiabatic Control

There are two rather obvious methods available for preventing heat interchange between a body or system and its surroundings; these depend on (1) complete insulation, or (2) maintenance of the temperature of the environment of the body equal at all times to that of the body itself. The first method is open to the objection that there is no available insulating material which is anywhere near perfect, and is subject to the disadvantage that when the temperature of the insulated body is changing the insulator introduces a capacity factor which is hard to evaluate. For example: a Dewar flask, which is the best insulating container we have, will exchange heat with its environment at rates even greater than those observed for coal heating in storage. Clearly such an insulator is inadequate for protection of coal under study in the laboratory against heat exchange. Further, any spontaneous heating of a substance contained by a Dewar flask must involve heating of the flask walls which requires that heat be supplied by the substance. The heat so required is difficult to determine and this renders uncertain the estimation of that part of the change in temperature due to spontaneous heating of the substance. For the purpose here, method (2) would be ideal if it were possible to effect absolute temperature control, in which case there could be no heat interchange between the coal and its environment, and the heat capacity of containers would not enter as with method (1). Unfortunately, absolute control is unattainable, and the question to be decided is, can it be made precise enough for the problem at hand?

The precision required is obviously dependent upon the magnitude of the heating rates which it is desired to study. At low temperatures the heating rate of coal is very low and a high precision of temperature control is therefore required if the observed heating rate is to be significant—if it is precise enough to answer the question, for example, as to how fast a coal will heat spontaneously at room temperature. A rough idea of the required precision may be gained by examination of statistics[1] indicating how long it takes coal in storage to fire spontaneously. Thus for a number of cases of spontaneous combustion, eight weeks were required for the temperature to rise to the smoking point, say 300 °C, which, if the rate were uniform, would fix it at 0.22°C per hour. Of course, the rate is not uniform, but one would judge from these considerations that the required precision is something better than 0.22°C per hour. On the other hand, heat may well have been conducted away from the coal piles at rates greatly exceeding 0.22° per hour, which would require that the heating rate chargeable to self-heating of the coal be much larger. The problem may be studied by determining the rate of self-heating in an adiabatic calorimeter. The apparatus finally developed by the writers gave adiabatic control good to approximately 0.15° per hour and this was sufficiently close to give positive indication of self-heating in coal at temperatures around 50°C.

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[1] H. H. Stoek, C. W. Hippard, and W. D. Langtry, *loc. cit.*

Apparatus and Experimental Method

Figure 1 shows the apparatus used in this work. Referring to the figure; (*a*) is a Dewar flask holding approximately 4 liters of transformer oil in which is immersed the vacuum jacketed glass tube *b* for holding about 30

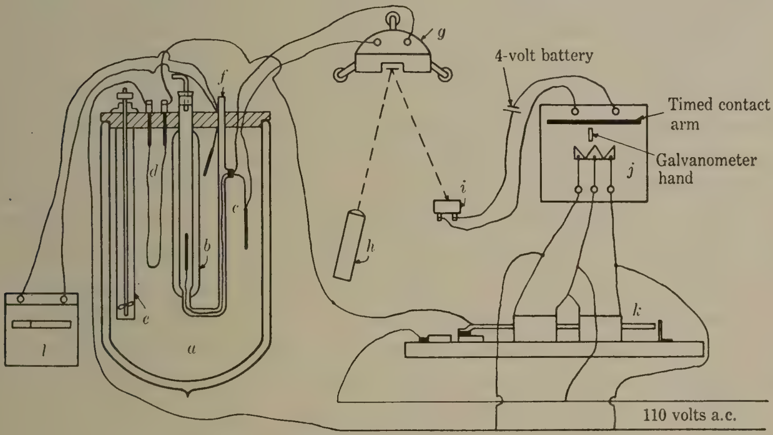

FIG. 1.—Apparatus for adiabatic control.

grams of the coal under investigation. Connected to the bottom of this tube is a $^1/_4$-inch branched tube which serves to admit oxygen to the coal and also the controller thermel *c*. This last is made up of 24 copper-constantan elements in series giving an e. m. f. of approximately one microvolt per 0.001°C differential between the oil bath and the coal sample.

Attached to the wood cover of the flask *a* is the turbine stirrer *e* and the nichrome heating coil *d*. A Siemens and Halske temperature recorder *l* serves to record the temperature of the oil bath. The arrangement of the thermel *c* is such that it is entirely immersed in the oil bath which is of uniform temperature closely approximating that of the coal at all times. Therefore, the temperature of the junctions cannot be greatly affected by conduction of heat along the connecting wires. The thermel is connected to a high-sensitivity reflecting galvanometer *g* (sensitivity 3 millimeters per microvolt, meter scale) which reflects a beam of light from the lamp *h* to the sensitive surface of a selenium cell *i*. This cell is connected through a 4-volt battery to the Thwing thermoelectric controller or relay *j* which is essentially a pointer galvanometer equipped with a periodic contact device actuated by clockwork. This forces a small block carried by the pointer to close one of two electric circuits every 5 seconds. These circuits are connected with the double relay *k* which opens and closes the heating circuit to the coil *d* in the oil bath. The function of this rather complicated system of relays is of course to make the controller thermel actuate the bath heating coil for the smallest possible temperature difference between coal and oil and with the minimum time lag. With the present arrangement 0.013 °C temperature difference is sufficient to actuate the heater and the time lag is about 15 seconds or somewhat less than that of a Beckman differential thermometer.

There are several methods of increasing the temperature sensitivity of this apparatus, perhaps the easiest being to increase the length of the beam of light reflected by the galvanometer to the selenium cell. The cell is actuated by lateral displacement of the beam on and off its sensitive surface and lengthening the beam will increase the displacement in direct proportion to the beam length for a given angle of galvanometer deflection. There is an optimum length of beam, however, beyond which the stability of the galvanometer system is insufficient to give positive displacements. The zero shift becomes of the same order of magnitude as the least effective displacement. Further, with excessive length of beam absorption of light by the air becomes appreciable and it will not have sufficient intensity to properly operate the cell. Other ways of increasing the sensitivity are: substitution of a more sensitive galvanometer and increasing the number of elements of the thermel. Without going into the limitations of the several ways of increasing sensitivity it will be sufficient to observe that with this apparatus a sensitivity as great as 0.002° to 0.005° is attainable. However, in order to utilize such a high sensitivity the various lag factors of the apparatus would have to be made much smaller than the writers have been able to make them so far.

One of the most troublesome lag effects is introduced through variation in the amount of heat required by the oil bath. Thus when the coal is heating slowly as at low temperatures the oil bath requires very little heat and its rate of input may be so adjusted as to correct largely for the lag of the electric controller. This adjustment, however, will not hold for higher temperatures where the coal is heating rapidly and the radiation from the oil bath is much greater. In spite of the fact that a temperature sensitivity of 0.013 °C was attained (and a higher sensitivity was easily attainable) owing to lag effects, the adiabatic control was not better than

0.15°[1] per hour. This means that for any given test run the recorded heating rate was subject to an error as large as 0.15° per hour.

Experimental Method

In order to eliminate thermal effects other than that due to oxidation of the coal tested fresh samples pulverized to 100 mesh and preserved in natural gas were first dried at 140° in a current of gas. This was the highest temperature reached in the test range, and it was necessary to have the coal dry at all lower temperatures, since otherwise moisture evaporating during the test would abstract heat (latent) from the system. The dried sample, about 35 grams, was allowed to cool and was then placed in the test apparatus, the oil bath being heated to a starting point previously fixed upon. This last was usually 50°C or 70°C.

A slow current of gas, dried over H_2SO_4 was now passed through the coal until it heated up to the temperature of the oil. This required from $^3/_4$ to $1^1/_4$ hours. After bringing the coal and oil to the same temperature the switches of the automatic adiabatic control were closed, and while the stream of natural gas was maintained a zero setting of the apparatus was obtained. The zero position of the reflected beam of light on the selenium cell was so adjusted as to correspond to zero e.m.f. of the control thermel so that for the smallest e.m.f. differential the cell would operate the relays to the oil bath heater. Since there could be no self-heating of the coal while kept in a dry inert atmosphere the whole system remained at constant temperature when perfect adjustment was secured. A Beckman thermometer reading to 0.01°C kept in the oil bath, served to indicate the temperature fluctuations, and it usually required several hours time with occasional temperature observations and several trial adjustments of the apparatus to get the system to equilibrium at constant temperature. After this had been accomplished the temperature recorder was started and the gas stream was replaced by a stream of dried oxygen from a closed circulating system at a rate of about 150 cc. per hour. It was found that at this rate the gas would be heated to the temperature of the oil bath on passing through the immersed intake. Further, the gas after passing through the coal still contained 60 to 80 per cent oxygen, showing that there was sufficient excess for the oxidation reactions. The coal was allowed to heat under the above conditions until the temperature rose to 130 to 140°C or well above that considered dangerous in coal storage. This required from 12 to 48 hours, depending on the kind of coal and the initial temperature. There being no interchange of heat between the coal and its surrounding and no appreciable loss or gain by latent heat of vaporization, the rate of heating shown by the recorder was taken as directly proportional to the intensity of self-heating of the coal over the temperature range studied.

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[1] Since this was written control good to 0.015° per hour has been realized.

Character of Spontaneous Heating

Figure 2 shows the rise in temperature with time for two coals—lignite and peat—when allowed to heat spontaneously in the apparatus described above. Under the conditions prevailing all variables known to influence self-heating in a coal pile have been eliminated except that due to variation in the coal composition. The coals tested were sized to 100-mesh. If they had been coarser the heating rates undoubtedly would have been smaller thus flattening the curves but not changing their general trend. Fine coal was chosen for testing because it oxidizes faster than coarse coal and by such choice the observation time could be reduced to a minimum and small errors in adiabatic control had a minimum effect. Curves 1 and 2 represent duplicate runs on an Illinois coal; curve 3 represents a single run on lignite; curves 4, 5, 6, apply to runs on Pittsburgh coal for different starting temperatures. The heating of a sample of peat is also indicated in the figure.

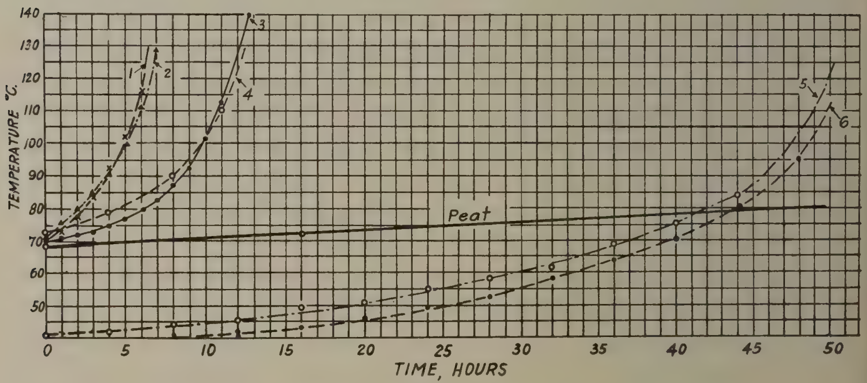

FIG. 2.—Spontaneous heating of dry powdered coal in dry oxygen.

Of the samples tested, Illinois coal oxidizes most rapidly, that is, it has the most rapid heating rate, and peat most slowly. In fact the result for peat may be taken to mean that compared with coal it is not subject to spontaneous heating at all. On examination of the coal and lignite curves, particularly curves 5 and 6, it will be seen that the rate of spontaneous heating is a function of the temperature; that is, the higher the temperature, the more rapid the heating rate. All coals so far tested show this general characteristic and the curves are very similar in shape over corresponding temperature ranges where the same scale is used in plotting. Peat shows a constant heating rate within the temperature range where it was tested and differs in that respect from coals which are known to heat spontaneously. The writers suggest, therefore, that the main characteristic of spontaneous heating is that the rate of heating is an increasing function of the temperature. All organic materials which heat in this manner would be expected ultimately to fire spontaneously under favorable conditions; that is, provided a sufficient air supply and not too rapid escape of the heat generated. Experience teaches us that some organic materials fire spontaneously and some do not. The reason for this would logically be sought in differences in chemical constitution—but the constitution of such substances as coal and peat is not known. One distinguishing characteristic between the two kinds of materials apparently lies in the difference in character of their heating rates. Suffice it to say now that the characteristics noted seem to apply generally and to represent with fair accuracy the rate of oxidation of dry pulverized coal when adiabatic conditions are maintained. With a view to clearer exposition of the facts involved the mathematical treatment which follows was applied to curve 5.

The emprical formula[1] $\Theta = K\dfrac{(a + T)}{(b - T)}$ was found to fit the curve at all points within the limits of experimental error. In the formula Θ = temperature, T = time and K, a and b are constants. The values of these constants for this particular curve are: −26.27, −103 and 61.74 respectively; for the similarity of this curve to those for other coals it may be assumed that with proper constants the formula has general application. Analysis of the formula shows that:

(1) When $b = T = 61.7$, Θ = infinity; which means that it will take 61.7 hours heating from the starting point (42°C) before ignition takes place. From the plotted portion of the curve it will be seen that this may well be true.

(2) On making T equal to −infinity it will be seen that the expression takes the indeterminate form $K\dfrac{-\text{infinity}}{+\text{infinity}}$ which may be evaluated, however, by differentiating numerator and denominator of the fractional part with respect to T. This gives $K\dfrac{(-1)}{(+1)} = \Theta = 26.27°$, which means that at some time T is negative (out of the range of the plot) a limiting temperature (26.27) is reached below which spontaneous heating does not occur. Experimentally, spontaneous heating could not be started below 37°C, which indicated that a lower limiting temperature does actually exist.

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[1] Choice of an appropriate time-temperature scale is necessary in plotting; otherwise important characteristics of the function may be masked. For the work here unit time is taken as 1 hour and unit temperature corresponding is taken as 5°C.

(3) From the equation $\Theta = K\frac{(a+T)}{(b-T)}$, making Θ equal to 26.27, the temperature below which there is no heating, and solving for T, the equation becomes $\frac{a+T}{b-T} = -1$, from which, with the substitution of the values found for the constants, $-T$ equals -82.3 hours; which means that starting from a temperature of 26.27°C it would require 82.3 hours for the system to heat to 42°, from which time was measured in the plot.

(4) From (1) and (3) it is seen that the time required for the coal to heat spontaneously from 26.27° (the point where heating starts) to the ignition point is: 61.74 + 82.3 equals 144 hours.

Summary

1. An adiabatic calorimetric apparatus was developed by means of which the spontaneous heating characteristics of fine dry coal could be studied so as to obtain a direct measure of the rate of spontaneous heating at different temperatures, uninfluenced by various heat interchange factors—such as conduction, ventilation and latent heats—known to effect the heating of coal in storage.

2. Specimen time-temperature heating curves in pure oxygen are given which show very nearly the same rate of heating intensities over corresponding temperature ranges for all coals studied where true spontaneous heating took place; the curves all have the same general trend.

3. A heating curve for Pittsburgh coal was treated mathematically and it was shown that under adiabatic conditions and in an atmosphere of oxygen:

(*a*) The coal would start heating at a temperature of 26.27°C; no heating would take place below that temperature.

(*b*) Using the experimental data of the plot and that calculated by means of the formula, the time required for dry Pittsburgh coal to heat from the lowest temperature at which heating would develop to the ignition temperature was 144 hours, adiabatic conditions being maintained and dry air being used.

Acknowledgments

The writers wish to acknowledge indebtedness to R. E. Hall, Physical Chemist, Pittsburgh Station for very material assistance in developing the mathematics of the paper, also to O. P. Hood, Chief Mechanical Engineer, and to A. C. Fieldner, Supervising Chemist, under whose direction the work was carried out.

COAL AND COAL PRODUCTS LABORATORY
CHEMICAL DIVISION
PITTSBURGH EXPERIMENT STATION
BUREAU OF MINES

COMPARISON OF METHODS OF ANALYSIS OF GYPSUM[1]

By P. P. Budnikoff

(Translated from the Russian by W. M. Sternberg)

ABSTRACT

The different analytical methods proposed for the evaluation of gypsum have been subjected to an experimental test. A combination method, consisting of a fusion with $KHCO_3$ and determination of CaO by $KMnO_4$ titration, the SO_3 by Andrews' method of titration of $BaCrO_4$, has been found to give very reliable results with the least consumption of time.

Introduction

Gypsum is acquiring of late an ever-increasing importance in construction work. In connection with this there has been made a number of attempts to work out standard methods for testing of gypsum. W. E. Emley and C. F. Faxon[2] propose to compute the relationship between the resistance to compression and stretching and the gypsum contents. Believing such methods to be of great importance and wishing to work out reliable methods of chemical analysis of gypsum we have attempted to work out a standard method and compare results. As raw material we have first used Kahlbaum's c. p. $CaSO_4.2H_2O$ and later we have extended the work to industrial gypsum.

Ammonium Carbonate Method

This method is based on the transformation of gypsum in water into $CaCO_3$ solution by means of ammonium carbonate, in accordance with the reactions $CaSO_4 + (NH_4)_2CO_3 = CaCO_3 + (NH_4)_2SO_4$. $CaCO_3$ being the less soluble the reaction proceeds from left to right. The interaction takes place rapidly at first but the end is only reached in 15–20 hours with frequent stirring.

The sample of gypsum is placed into a 200-cc. Erlenmeyer flask containing a saturated solution of $(NH_4)_2CO_3$. The mixture is shaken for one-half hour and then permitted to stand for 24 hours. The precipitate is filtered off, carefully washed with water on the filter paper and the SO_4 is determined in the filtrate by precipitating with $BaCl_2$, after acidifying with hydrochloric acid. The precipitated $CaCO_3$ on the filter paper is

Results of Analysis

	Found		Calculated
	I	II	
CaO	33.07%	33.01	32.56
SO_3	46.78	46.56	46.52
H_2O	20.82	20.80	20.92
	100.67	100.37	100.00

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[1] Recd. June 14, 1924.

[2] "Results of Testing of Gypsum Products," *Jour. Amer. Ceram. Soc.*, **3** [12], 984–93(1920).

dissolved with HCl and the CaO in it determined gravimetrically by precipitation with $(NH_4)_2C_2O_4$.

A small error tending to increase CaO may be due to the fact that part of $CaSO_4$ resists decomposition. To obtain the best results an excess of $(NH_4)_2CO_3$ must be used and the samples taken should not be greater than 0.3–0.4 gm.

The residue on the filter paper may consist not only of $CaCO_3$ but also of $Fe(OH)_3$ and $Al(OH)_3$ when industrial gypsum is analyzed. In that case upon dissolving the precipitate, Fe^{+++} and Al^{+++} are first precipitated in the usual way with NH_4OH and later on the Ca^{++}.

Fusion Method

The sample of gypsum is fused with 5–6 times its weight of $NaKCO_3$, dissolved in water, the $CaCO_3$ separated from Na_2SO_4 by filtration of the cold solution and CaO and SO_3 determined as above.

RESULTS

	Found	Calculated
CaO	32.44	32.56
SO_3	46.70	46.52
H_2O	20.89	20.92
	100.03	100.00

The insoluble residue obtained with industrial gypsum upon decomposing the melt with water may contain $Al(OH)_3$, $Fe(OH)_3$ and insolubles. The SO_3 is determined in the water extract in the usual way and Fe_2O_3, Al_2O_3 and CaO determined in the water insoluble residue.

Determination of Sulphuric Acid According to Raschig[1]

This method is based on the slight solubility of benzidine sulphate $NH_2.C_6H_4.C_6H_4.NH_2.H_2SO_4$ and on the strong hydrolysis of salts formed by the union of strong acids with weak bases. Benzidine sulphate, $C_{12}H_8(NH_2)_2.H_2SO_4$ is broken up into benzidine and free sulphuric acid which is titrated with $N/10$ NaOH in presence of phenolphthalein. The formation of benzidine sulphate and its hydrolysis take place in accordance with the equations:

1. $C_{12}H_8(NH_2)_2.2HCl + CaSO_4 = C_{12}H_8(NH_2)_2.H_2SO_4 + CaCl_2$
2. $C_{12}H_8(NH_2)_2.H_2SO_4 + 2H_2O = C_{12}H_8(NH_2)_2.2H_2O + H_2SO_4$

A sample of gypsum of about 0.2 gm. is dissolved in 150–200 cc. of boiling water. The cooled solution of the sulphate is added with stirring to the benzidine solution. For the given weight of sample 200–300 cc. benzidine hydrochloride are taken. The precipitated $C_{12}H_8(NH_2)_2H_2SO_4$ is filtered off, washed, transferred with the filter paper into a flask with water, heated to 50–60°C and titrated with $N/10$ NaOH.

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[1] *Z. für ang. Chem.*, **617**, 818(1903); *Z. f. anal. Ch.*, **42**, 477(1903).

RESULTS OF ANALYSIS: SO_3, found, 45.69; 45.52; 45.54; 46.23%. Calculated, 46.52%.

Raschig's method deserves attention because of its rapidity.

Determination of Sulphuric Acid According to Andrews[1]

This method is based on the solubility of $BaCrO_4$ in hydrochloric acid while $BaSO_4$ is practically insoluble. By adding $BaCrO_4$ suspended in water to a hydrochloric acid solution of the sulphates we precipitate the barium in the form of $BaSO_4$ and subsequently we precipitate $BaCrO_4$ after neutralizing the solution. The amount of chromic acid left in solution is equivalent to the amount of sulphuric acid originally present. The amount of chromic acid is determined iodometrically by titration with sodium thiosulphate and the SO_3 calculated from the analytical results.

The sample of gypsum is dissolved in 10 cc. of hydrochloric acid, sp. gr. 1.17, 6 cc. $BaCrO_4$ suspended in water are added and the mixture heated 15–20 minutes. Upon cooling the solution is neutralized with ammonia to a weakly alkaline reaction. The solution and precipitate are transferred to a 250-cc. measuring flask, diluted to the mark and filtered. One gram KI is added to 100 cc. of the solution, acidified with 5 cc. concentrated HCl, the flask covered and permitted to stand for 20 minutes, after which the separated iodine is titrated with $Na_2S_2O_3$ solution in the presence of starch.

RESULTS OF ANALYSIS: SO_3, found, 46.63%; 46.50%. Calculated, 46.52%.

Andrews' method appears to be fully reliable and easy of execution.

Titration Method with $KMnO_4$[2]

This method is based on the reaction:

$$2KMnO_4 + 5CaC_2O_4 + 8H_2SO_4 = 5CaSO_4 + 2MnSO_4 + K_2SO_4 + 10CO_2 + 8H_2O$$

0.2 gm. gypsum are dissolved in 20 cc. of moderately strong HCl, diluted with 100 cc. water and made weakly ammonical with ammonia. The solution is heated to boiling and precipitated with a boiling solution of $(NH_4)_2C_2O_4$ added drop by drop. The precipitate is permitted to settle for 1–2 hours, filtered through an ashless filter, washed first with a solution of $(NH_4)_2C_2O_4$ and later with water. The CaC_2O_4 is transferred with the filter paper into a 500 cc. Erlenmeyer flask, 250 cc. water and 5 cc. concentrated H_2SO_4 are added, heated to 70°C and titrated with $N/10$ $KMnO_4$.

RESULTS OF ANALYSIS: CaO, found, 32.38; 32.48%. Calculated, 32.56%.

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[1] *Amer. Chem. Jour.*, **2**, p. 567.

[2] "Classen Ausgewählten Methoden der Analytischen Chemie," Bd. I, 794(1901).

This method of determination with $KMnO_4$ has all the advantages over other methods in accuracy and speed.

By combining Andrews' method with that of titration with $KMnO_4$ the following results had been obtained:

	Found	Calculated
CaO	32.68	32.56
SO_3	46.15	46.52
H_2O	20.90	20.92
	99.73	100.00

Analysis of Commercial Gypsum, $CaSO_4.1^1/_2H_2O$

We have analyzed industrial gypsum by the method of fusion and the combined Andrews' and $KMnO_4$ method, with the following results:

Method	Sample, gm.	CaO, gm.	SO_3, gm.	%CaO	%SO_3	%H_2O	Total
Fusion	0.3024	0.1102	0.1543	36.44	51.02	10.77	98.23
Combined	0.1255 for CaO 0.1255 for SO_3	0.04585	0.06385	36.53	50.82	10.77	98.17

The table below summarizes all the results obtained:

No.	Method	Sample, gm.	CaO found, gm.	SO_3 found, gm.	CaO %	SO_3 %	H_2O %	Total
1	Ammonium	0.1690	0.0559	0.0791	33.07	46.78	20.82	100.67
2	Carbonate	0.1729	0.0571	0.0801	33.01	46.56	20.80	100.37
3	Fusion	0.2238	0.0726	0.1045	32.44	46.70	20.89	100.03
4	Raschig's	0.2001		0.09145		45.69		
5	Raschig's	0.2002		0.09113		45.52		
6	Raschig's	0.2004		0.09287		45.54		
7	Raschig's	0.2044		0.0945		46.23		
8	Andrews'	0.2104		0.0981		46.63		
9	Andrews'	0.2035		0.0946		46.50		
10	$KMnO_4$	0.2019	0.06538		32.38			
11	Titration	0.2102	0.06829		32.48			
12	Combination of	CaO 0.125 SO_3 0.125	0.04086	0.05267	32.68	46.15	20.90	99.73
	Calculated				32.56	46.52	20.92	100.00

Results obtained lead to the conclusion that for industrial purposes the combination of Andrews' and $KMnO_4$ titration method gives an entirely reliable and rapid analysis of gypsum for the determination of $CaSO_4$.

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THE DIRECT FIRED CAR TUNNEL KILN ON ROOFING TILE[1]

BY C. R. MINTON

ABSTRACT

The pioneer car tunnel kiln for the firing of roofing tile is described. The kiln is 324 feet, 11$^1/_2$ inches long and holds 52 cars each of which carries 2.3 tons of fired ware. Ten furnaces equipped with Maxon Premix combination oil and gas burners are used. A schedule of one car every 65 minutes is in operation, 56 hours and 20 minutes being required for a trip through the kiln. The ware reaches a maximum temperature of 1820°F and is drawn from the kiln at 400°F. Additional cooling is accomplished with a portable fan. The kiln has a capacity equal to ten 30-foot round down-draft kilns and shows a fuel saving over the latter of 64.2%. A total of 15 h. p. is required. A saving in setting and drawing labor of 29.2% and 45.8% respectively is effected.

Another milestone in the advance of the direct fired car tunnel kiln into the heavy clay wares field has been marked by the successful operation of the Harrop Car Tunnel Kiln for firing roofing tile which has recently been installed at plant No. 1 of the Los Angeles Pressed Brick Company of Los Angeles, California.

The kiln proper has a length of 324′ 11$^1/_2$″, a tunnel width of 4′ 10″, and an available setting height from car top to spring of arch of 4′ 11″.

The kiln holds fifty-two cars inclusive of one car in the charging vestibule. No discharge end vestibule is used. The refractory car top is 6′ 2$^1/_4$″ long and 5′ 2″ wide. Each car weighs 3610 pounds and carries a double deck or bench superstructure weighing 2450 pounds. These benches consist of fire clay slabs 3″ in thickness supported by 6″ x 6″ fire clay posts. The available setting space on the car top and each superstructure deck measures 5′ 10″ long and 4′ 4″ wide. Each car has a capacity of 766 pieces or 2.3 tons of burned ware.

An oil gear pusher moves the 554,320 pound train through the kiln, a total pressure of 18,000 pounds being required.

Along the firing zone of the kiln are ten furnaces, five on each side. Each furnace is equipped with a Maxon Premix combination oil and gas burner.

Special features of the kiln consist of a watersmoking device and two oxidation furnaces. The latter are located one on each side of the kiln approximately mid-way between the charging end and firing zone. These furnaces are only intended to be used when burning heavier wares such as brick, for which the kiln is also designed.

The kiln with its return and reserve tracks is housed in an Austin standard steel building 352 feet in length and 40 feet in width. The cost of this building erected complete on foundations in place was approximately $18,000.

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[1] Presented at the Atlantic City Meeting, Feb., 1924 (Heavy Clay Products Division).

The kiln is located at right angles to the tunnels of a waste heat drier (Fig. 1) and by means of turntables the cars of dried ware are placed upon a track which closely parallels the kiln car return track. The operation of setting is thus direct from the drier car to the kiln car. A clear space of thirty inches in width betweeen the drier cars and the kiln car has been found to be the most efficient for the transfer of ware. The setting zone occupies approximately the middle third of the kiln length and as soon as a car is loaded it is pushed by hand to the reserve zone near the charging end.

Under the present operation only four furnaces on each side are in use. These are fired with natural gas having a 1100 B.t.u. value.

At the present rate of production and operation one car is removed from, and one car is placed in, the kiln every 65 minutes. It is evident that this schedule can be reduced to one hour and perhaps less. On the 65-minute schedule a car passes through the kiln in 56 hours and 20 minutes. Of this time approximately 22 hours are required for watersmoking, and oxidation, 8 hours for actual firing and soaking, and the remainder in cooling.

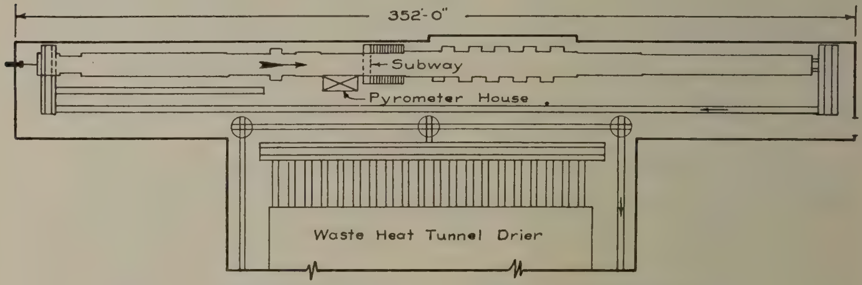

Fig. 1.—Harrop Tunnel Kiln, Los Angeles Pressed Brick Co.

In its passage through the kiln the ware reaches a maximum temperature of 1820°F as recorded by the thermocouple in the crown. On the car cone 04 is down.

Characteristic of this design of car tunnel kiln, the bottom exhibits a tendency to become hotter than the top. However, the top temperature can easily be evened to that of the bottom by a slight upward inclination of some of the burner nozzles. Since the market demands a variation in shades the bottom tiles are generally burned harder than the top.

It has been found best to draw the ware from the kiln while it is at a temperature of about 400°F. In order to cool it to a handling temperature and keep pace with the unloading, a cool air blast from a portable fan is turned upon the ware soon after it is removed from the kiln.

With one handling the cooled ware is unloaded from the kiln car, sorted, graded, and stacked upon trailers which are hauled by gasoline trucks to the storage yard.

With an average output of 2.3 tons of burned ware per car, the 65-minute schedule produces 51.60 tons per day or 1548 tons per 30-day month, which is practically equal to the average monthly production of ten thirty-foot round down-draft kilns which totals 1660 tons.

The best monthly average of first quality ware has been 94.2 per cent.

Twenty-five hundred cubic feet of natural gas is consumed per ton of fired ware as against 7000 cubic feet per ton in a thirty-foot round down-draft kiln. This is a direct fuel saving of 64.2 per cent.

The electric power required by the kiln includes a 15 h. p. draft fan motor, a 15 h. p. pressure fan motor, ten $^1/_2$ h. p. burner motors, and a pusher motor of $^3/_4$ h. p., or a total of $35^3/_4$ h. p.

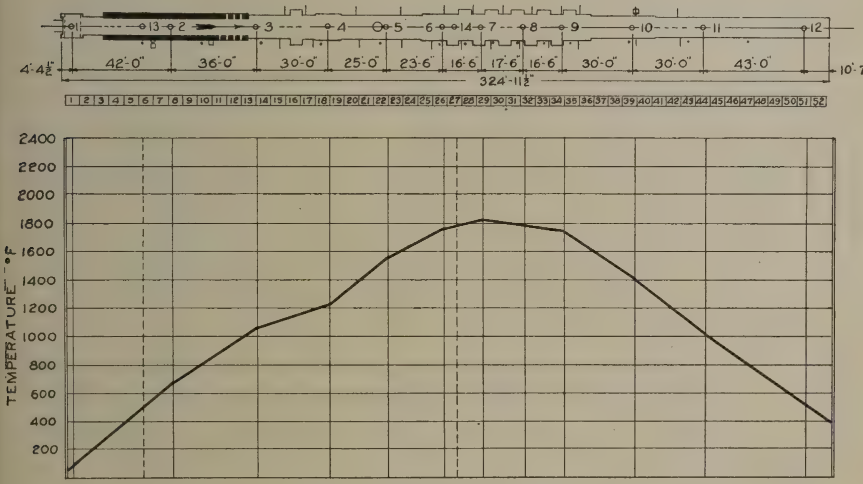

FIG. 2.—Temperature record.

The charging, firing and drawing of the kiln are handled by one burner. Any assistance needed in moving of cars, etc. is called from general labor.

Setting the kiln cars requires 2.14 labor hours per ton of burned ware while the setting of a thirty-foot round down-draft kiln requires 3.02 labor hours per ton. Drawing or unloading the kiln cars requires 1.06 labor hours per ton while drawing a thirty-foot round down-draft kiln requires 1.96 labor hours per ton. The labor saving in setting and unloading is 29.2 per cent and 45.8 per cent respectively.

Recently an experimental setting car caused a wreck which required the shutting down of the kiln for its removal. After three months' continuous operation the interior of the kiln was found to be in perfect condition and the exterior exhibited only a few small cooling cracks. The expansion joints had functioned perfectly.

LOS ANGELES PRESSED BRICK CO.
LOS ANGELES, CALIF.

AVENTURINE GLAZES[1]

By V. K. Haldeman

Introduction and Historical

The production of an aventurine effect consists in the addition of a metallic oxide to the glaze in such quantities that, when heated to a molten mass, the glaze matrix becomes saturated and as the glaze cools, supersaturation results, with the ultimate precipitation of thin plate-like crystals or spangles.

The oxides most commonly used for this purpose are those of iron, chromium and copper.[2] The oxide is not always used. For instance, in the case of iron aventurines, finely powdered iron, ferrous oxide, ferric oxide and ferrous sulphate have all been used with some degree of success.

According to the statement of Wohler,[3] a chrome aventurine may be produced by a mixture of kaolin 31 parts, quartz sand 43 parts, gypsum 14 parts, and ground porcelain 12 parts. This is finely ground and mixed with 300 parts of water. To the glaze slip is added 19 parts of potassium dichromate, 47 parts of sugar of lead, and 100 parts of iron vitriol (ferrous sulphate) and as much ammonia as is necessary to completely precipitate the iron. By repeatedly washing with water, the glaze is freed of the potassium and the ammonium salts. It is applied in the usual manner, and burned in a porcelain kiln.

Mackler[4] used Wohler's formula, but obtained no satisfactory results. However, by covering the trial pieces thus obtained with an easily flowing lead glaze, he succeeded in producing a dark colored glaze mass penetrated with crystals.

He treated a glaze of the following formula:

$$\left.\begin{array}{l} 0.25\ K_2O \\ 0.25\ Na_2O \\ 0.50\ CaO \end{array}\right\}\ 0.75\ B_2O_3 \quad 2.25\ SiO_2$$

with increasing amounts of chromic oxide, and found that a glaze containing 2% chromic oxide showed groups of beautiful glittering crystal flakes. In glazes of higher chromic oxide content the precipitate appeared in increasing amounts, and with 6% chromic oxide, the crystals had formed in masses. In order to bring about an equal distribution of the flakes, he treated the 2% chromic oxide containing glaze with 3% charcoal, by which was produced a strong boiling effect and intimate mixture of the molten mass.

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[1] Report on an investigation undertaken to satisfy in part the requirements for the degree of B.S. in Ceramic Engineering at the University of Illinois. Recd. May 2, 1924.

[2] C. W. Parmelee and John Lathrop, "Aventurine Glazes," *Jour. Amer. Ceram. Soc.*, **7** [7], 567(1924).

[3] Wohler, *Sprechsaal*, **29**, 463–4 (1896).

[4] Mackler, *Tonind. Ztg.*, 219 (1896).

He next treated the easily flowing glaze, of same formula given above, successively with 25% ferric oxide, 15–20% powdered iron, 25.8% FeO, and finally with 12.9% FeO and 14.3% Fe_2O_3. In each case an aventurine effect was produced. Treating with ferric oxide alone gave grayish metallic light crystal flakes; with 15–20% powdered iron, a transparent yellow glaze penetrated by innumerable golden yellowish flakes; FeO alone, a transparent yellow glaze with crystal flakes; the combination of ferrous and ferric oxides, a very beautiful transparent aventurine glaze, penetrated evenly by glittering flakes.

Mackler[1] also attempted the production of a copper aventurine by adding 5% Cu_2O and FeO to the base glaze already given, but received only a transparent green glaze.

Petrik[2] found that by melting dehydrated iron vitriol and common salt together, flakes of iron oxide are produced which dissolve only with very great difficulty in molten glass, and give accordingly an aventurine formation. He glazed the trial pieces twice, first with the normal glaze mixed with crystalline ferric oxide, and afterwards with an easily flowing transparent yellowish brown-lead glaze.

He imitated a chrome aventurine by first covering the trial pieces with the glaze containing crystalline ferric oxide and placing over this a greenish copper-lead glaze.

Another German investigator[3] has found that crystalline deposits in glazes may be obtained by saturating the glaze with the oxide and then adding an excess in crystalline form. The crystalline oxides are prepared by heating iron alum, manganese sulphate or chrome alum or potassium dichromate with equal parts of cooking salt in a refractory crucible to the strongest kiln temperature.

He gives the following as a suitable glaze:

Cryst. borax	38.2 parts	Quartz sand	120.0 parts
Calcium carbonate	10.0 parts	Oxide	x
Minium	70.0 parts		

where x may be 40 parts of ferric, manganese or chromium oxide. The glaze mixture is composed of 250 parts frit and 12.9 parts kaolin. This is ground finely and treated with 2 to 10% of the crystallized oxides. The firing temperature lies between cone 09 and cone 2.

Another German investigator[4] recommends this glaze as a good iron aventurine answering to all the requirements:

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[1] Mackler, *Sprechsaal,* **29,** 491 (1896).

[2] Petrik, *Sprechsaal,* **29,** 548–9 (1896).

[3] *Sprechsaal,* **40,** 329–30 (1907).

[4] *Sprechsaal,* **33,** 1671 (1900).

Sand	444 parts	Feldspar	13 parts
Borax	330 parts	Potassium nitrate	38 parts
Ferric oxide	148 parts	Barium carbonate	27 parts

Frit all ingredients. Grind finely and use without further additions.

Riddle[1] made a good aventurine by supersaturating the following frit with some coloring oxide, ferric oxide working especially well, giving a rich red color:

$$\left.\begin{matrix} 0.25\ K_2O \\ 0.25\ Na_2O \\ 0.50\ CaO \end{matrix}\right\} 0.75\ B_2O_3 \quad 2.25\ SiO_2$$

BATCH WEIGHT

Potassium nitrate	13.95 parts	Borax	26.38 parts
Calcium carbonate	13.81 parts	Flaky boric acid	8.53 parts
Flint	37.29 parts		

This glaze has the same formula as the glaze used by Mackler.

Scope of Present Investigation

The object of this study was to determine the effect of substituting chromic oxide for ferric oxide and alumina in a cone 02 aventurine glaze. As an aid in the development of such an aventurine, the substitution of lithium oxide for sodium oxide in the RO member was also investigated, as well as the effect of variation in the boric oxide content. An attempt was made also to ascertain the heat treatment which promoted development of crystallization to the greatest degree.

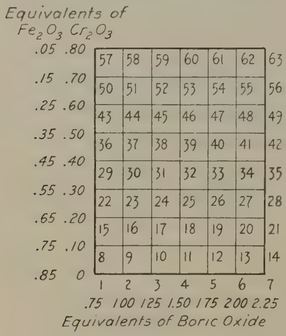

FIG. 1.

Method of Investigation

The study was divided into four series:

1. Using a cone 02 iron aventurine as a base glaze, chromic oxide was substituted for ferric oxide in such a manner as to maintain the sum of the two constant (0.85) equivalents but allowing the iron oxide to vary between .05 and .85 equivalents and the chromic oxide between zero and .80 equivalent. The boric oxide was made to vary between .75 and 2.25 equivalents.

The field of investigation was laid out on a rectangular diagram as shown (Fig. 1).

The base glaze selected for this series was:

$$1\ Na_2O \quad \left\{\begin{matrix} 0.1\ \ Al_2O_3 \\ 0.85\ Fe_2O_3 \\ 1.5\ \ B_2O_3 \end{matrix}\right. \quad 6\ SiO_2$$

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[1] F. H. Riddle, "A Few Facts Concerning the So-called Zinc Silicate Crystals," *Trans. Amer. Ceram. Soc.*, **8**, 336 (1906).

2. In an effort to counteract the marked tendency of chromic oxide to increase the refractoriness and viscosity of the glaze, and consequent retarding the formation of aventurine crystals, it was decided to substitute lithium oxide for sodium oxide in the RO member. Lithium is an active flux of very low molecular weight. According to Stull[1] this should make lithium a good base for promoting crystallization.

To further decrease the refractoriness of the glaze, its flint content was reduced to four equivalents, and the sum of the iron and chromic oxides was cut down to a constant of 0.75 equivalent, instead of 0.85, as in the previous series. The boric oxide was held at 1.5 equivalents.

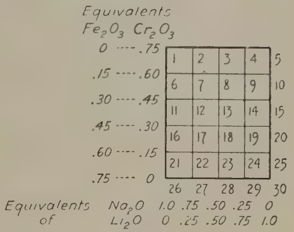

FIG. 2.

The glaze as finally corrected had this composition:

$$\begin{matrix} 0\text{–}1\ Na_2O \\ 0\text{–}1\ Li_2O \end{matrix} \quad \left\{ \begin{matrix} 0.1\ Al_2O_3 \\ 0.0\text{–}0.75\ Fe_2O_3 \\ 1.5\ B_2O_3 \\ 0.0\text{–}0.75\ Cr_2O_3 \end{matrix} \right. \quad 4\ SiO_2$$

and the field studied is shown in Fig. 2.

3. Maintaining a constant chromic oxide content of 0.1 equivalent, the effect was studied of varying the ferric oxide between 0.65 and 0.90 equivalents, against boric oxide between 1.25 and 2.0 equivalents (Fig. 3).

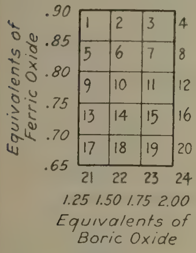

FIG. 3.

$$1\ Na_2O \quad \left\{ \begin{matrix} 0.1\ Cr_2O_3 \\ 0.65\text{–}0.90\ F_2e_3O \\ 1.25\text{–}2.0\ B_2O_3 \end{matrix} \right. \quad 4\ SiO_2$$

4. Using the same base glaze, the chromic oxide was reduced to a constant of 0.05 equivalent, and the ferric oxide and boric oxide varied as before.

The accompanying rectangular field represents the variations in these constituents for both Series III and IV.

Firing

Mellor[2] has shown that there are certain zones of crystallization, during the cooling of a glaze, in which crystallization proceeds with the greatest ease. These vary so widely with different glaze compositions that experiment is necessary to determine the correct zone of crystallization for any particular glaze. Mellor has further shown that, by rapid cooling of the glaze, it is possible to pass through such a zone without the production of crystals.

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[1] R. T. Stull, "Notes on the Production of a Crystalline Glaze," *Trans. Amer. Ceram. Soc.*, **6,** 186 (1904).

[2] J. W. Mellor, "Clay and Pottery Industry," pp. 60–61.

Following out these observations, several different heat treatments were tried, to determine the firing temperature and the rate of cooling which promoted maximum crystallization. The firing curves are shown in Figs. 4 to 10.

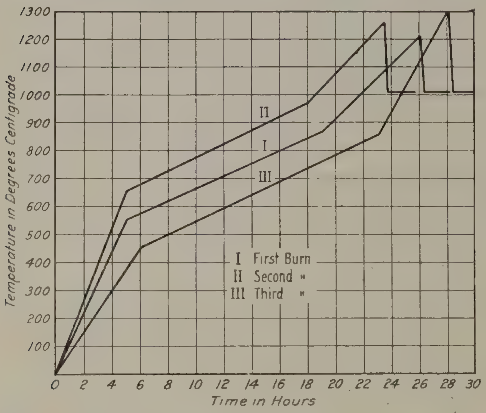

FIG. 4.—Time-temperature curves for aventurine glazes burned in electric furnace.

For Series I, seven different firings were made. They were as follows:

(1) At cone 6 (Fig. 5). Held for two hours at 1100°C. For this burn the gas-fired test kiln was used.

(2) At 1200°C (Fig. 4) in the electric furnace. Held for 2 hours at 1000°C.

(3) At 1250°C (Fig. 4) in the electric furnace. Held for 2 hours at 1000°C.

(4) At 1300°C (Fig. 4) in the electric furnace. Held for 2 hours at 1000°C.

(5) At cone 1 (Fig. 6) in Caulkins Revelation Kiln. Held for 2 hours at 900°C.

(6) At cone 02 (Fig. 7) in Caulkins Revelation Kiln. Held for two hours at 1000°C.

(7) At cone 02 (Fig. 8) in Caulkins Revelation Kiln. Allowed to cool, without any attempt to hold it at a particular temperature.

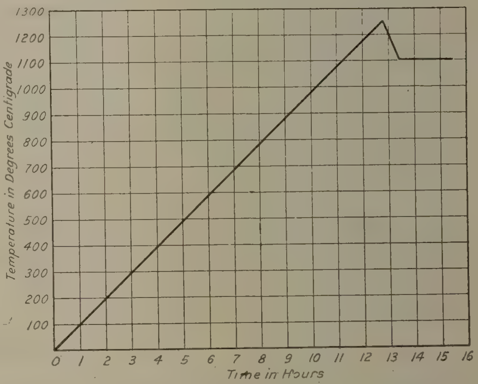

FIG. 5.—Time-temperature curve for aventurine glazes burned at cone 6 in gas test kiln.

Oxidizing conditions were maintained throughout each firing. Except in the electric furnace, cones were placed in various parts of the kiln to indicate the heat treatment of each glaze.

For Series II, one firing was made; *i. e.*, at cone 1 in the Caulkins Revelation Kiln (Fig. 6). Held for two hours at 900°C.

For Series III, two firings were made:

(1) At cone 02 (Fig. 9) in the Caulkins Revelation Kiln. Allowed to cool without holding at any particular temperature.

(2) At cone 02 (Fig. 7) in the Caulkins Revelation Kiln. Held for two hours at 1000°C.

For Series IV, two firings were made:

(1) At cone 02 (Fig. 8) in the Caulkins Revelation Kiln. Allowed to cool without regulation.

(2) At cone 02 (Fig. 10) in the Caulkins Revelation Kiln. Held for $^3/_4$ hour at 1050°, 1000°, 950°, 900°, 850°, 800°, 750° and 700°C.

Discussion of Results

Series I

The glazes containing only iron showed a tendency, especially with high B_2O_3 toward excessive crystallization; or, in fact, crystallization of the entire glaze mass, resulting in a rough matt effect not particularly pleasing nor desirable.

With the substitution of .10 equivalent of chromic oxide for a like amount of ferric oxide, the crystal growth was discouraged to such an extent that some of the glazes (those lowest in boric oxide) were entirely clear, while those high in boric oxide contained a large amount of very minute crystals evenly distributed, visible only on close examination. All of the glazes showed a high gloss.

Further increase of chromic oxide decreased the area of minute crystallization until, with more than .30 equivalent, only a clear brownish green or dark brown resulted.

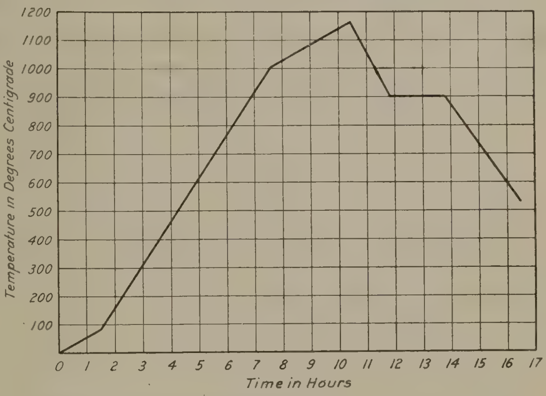

FIG. 6.—Time-temperature curve for aventurine glazes burned at cone 1 in Caulkins gas kiln.

Up to and including .30 equivalent chromic oxide the gloss was not measurably affected. Above this, however, the gloss was decreased, first with the glazes of low boric oxide content and finally with all. A chromic oxide content of .60 equivalent or more produced only dull glazes.

Above .40 equivalent chromic oxide crazing was prevalent, increasing with increasing boric oxide and chromic oxide. Crawling was noted in glazes high in chromic oxide.

A peculiar and rather attractive mottled effect was obtained in the low boric and chromic oxide area. The glazes had all the appearance of having crazed or separated into small blocks and then completely rehealed, but not sufficiently to obliterate the location of the original lines of separation.

Results obtained in different kilns and under different heat treatments varied but little. It was impossible to note any advantage gained by holding at various temperatures in cooling, nor by firing to higher temperatures. In fact, the best burn in the series was that at cone 02, cooled without regulation.

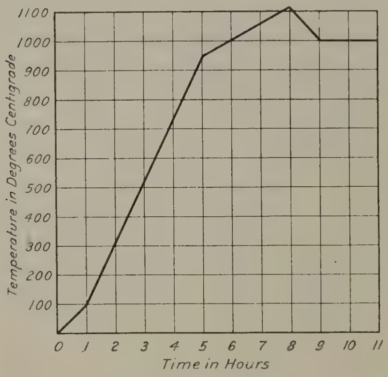

Fig. 7.—Time-temperature curve for aventurine glazes burned at cone 02 in Caulkins gas kiln.

Particularly in the glazes fired in the electric furnace, the higher temperature showed a marked tendency to promote the formation of metal-like splotches or scum on the surface of the glaze, and for this reason proved to be a positive detriment. The trial pieces fired in the electric furnace were stacked one above the other, and the bottoms of the pieces were covered with a thin glaze resulting from volatilization of the boric oxide.

Very attractive aventurines were obtained with:

$$Na_2O \qquad \left\{ \begin{array}{l} 0.1\ Al_2O_3 \\ 0.85\ Fe_2O_3 \\ 0.75\text{–}1.5\ B_2O_3 \end{array} \right. \qquad 6.0\ SiO_2$$

If applied on a flat piece, the glaze of low boric oxide content seems to be preferable, as there will otherwise be a tendency toward excessive crystallization and the consequent production of a matt. When applied on an upright surface, better results will be had if 1.25 to 1.5 equivalents of boric oxide are used. On an upright piece the crystals develop best when the glaze flows well. Too great fluidity gives a matt. The best results were obtained when the glaze was applied fairly thickly and evenly over the piece.

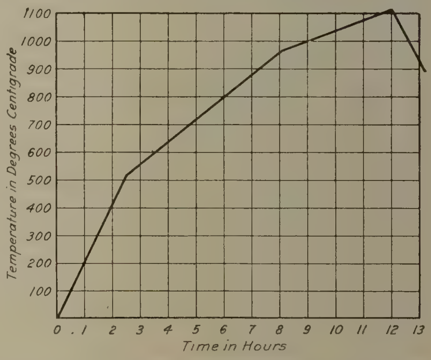

Fig. 8.—Time-temperature curve for aventurine glazes burned at cone 02 in Caulkins gas kiln.

Series II

The iron aventurine selected for this series was a dark brown-black glaze of high gloss, containing small but readily visible crystals thickly and uniformly distributed in the glaze matrix.

The substitution of lithium oxide for sodium oxide reduced the gloss, gave the glaze somewhat of a grayish cast, and decreased the crystallization. Further substitution caused a greater tendency in this direction, and .75 and 1.0 equivalents of lithium oxide gave semi-matt and matt glazes respectively.

With the substitution of .15 equivalent of chromic oxide for the same amount of ferric oxide, the growth of crystals was prevented entirely, with the exception of the glaze containing only sodium oxide, and here they were visible only when placed in strong light.

The best glazes were produced within the rectangle bounded by .15 to .45 equivalent chromic oxide and .5 to .75 lithium oxide. These were excellent matts, with an appearance like leather, due to the apparent division of the glaze into small patches. However, the glaze surface was intact and smooth. Glaze No. 13 (.45 Cr_2O_3 and .50 Li_2O) was the best of the group.

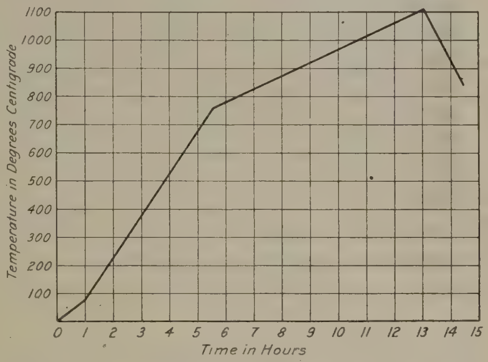

FIG. 9.—Time-temperature curve for aventurine glazes burned at cone 02 in Caulkins gas kiln.

High chromic oxide caused crazing, as did lithium oxide.

Glazes 1 to 15 fired at cone 6 were badly overfired, showing that lithium decreases the heat range very decidedly.

BATCH WEIGHTS

	Series 1				Series 2			
Extremes	1	2	3	4	1	2	3	4
Borax	143.3	382.0	382.0	143.3	286.5	...	...	286.5
Boric acid	...	31.0	31.0	...	...	186.0	186.0	...
Soda ash	66.3	...	...	66.3	26.5	...	...	26.5
Lithium carb.	...	...	...	...	...	74.0	74.0	...
Ferric oxide	136.0	136.0	8.0	8.0	...	...	120.0	120.0
Chromic oxide	...	...	121.6	121.6	114.0	114.0	...	...
Clay	25.8	25.8	25.8	25.8	25.8	25.8	25.8	25.8
Flint	348.0	348.0	348.0	348.0	228.0	228.0	228.0	228.0
	719.4	922.8	916.4	713.0	680.8	627.8	633.8	686.8

	Series 3				Series 4			
Extremes	1	2	3	4	1	2	3	4
Borax	238.8	382.0	382.0	238.8	238.8	382.0	382.0	238.8
Soda ash	39.8	...	...	39.8	39.8	...	...	39.8
Ferric oxide	144.0	144.0	104.0	104.0	144.0	144.0	104.0	104.0
Chromic oxide	15.2	15.2	15.2	15.2	7.6	7.6	7.6	7.6
Flint	240.0	240.0	240.0	240.0	240.0	240.0	240.0	240.0
	677.8	781.2	741.2	637.7	670.2	773.6	733.6	630.2

Series III

There were no pronounced variations in character of glaze. All glazes were dark brown in color, with uniformly distributed but very minute crystals, visible only on close examination.

The low boric oxide and ferric oxide gave highest gloss, while higher amounts of these oxides caused a roughening or dulling of the glaze, giving an appearance of immaturity. No variation in degree of crystallization could be observed. There was no crazing or crawling.

Two burns were made, one at cone 02, held at 1000° for two hours in cooling, a second at cone 02, cooled without regulation. Holding at 1000° was not conducive to better crystal development. On the other hand, it had a distinctly undesirable effect on the gloss. While the glazes, cooled directly, showed high gloss in the area lying between 1.25 to 1.5 equivalents of boric oxide, .65 to .85 equivalent of ferric oxide, holding the temperature produced a like gloss only at 1.25 equivalents of boric oxide and .65 to .80 equivalent of ferric oxide.

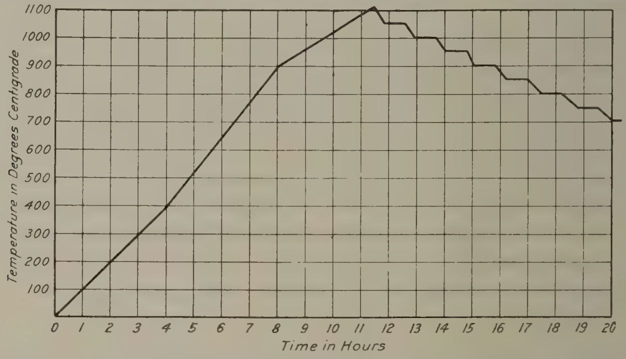

Fig. 10.—Time-temperature curve for aventurine glazes burned at cone 02 in Caulkins gas kiln.

Series IV

There was so little variation throughout the series that differentiation between the glazes would be difficult. The matrix was a dark brown color, of high gloss, in which were innumerable fine crystals, visible in ordinary light, which glistened brilliantly in sunlight. The crystals were uniformly distributed throughout the glaze mass.

The higher iron content produced a slightly darker brown color, and aided crystallization perceptibly. It was not possible to tell whether this was due to an increase in size of crystal, or only to the presence of a greater number of crystal faces.

Excepting for the fact that the low boric oxide glazes showed a mottled effect which was quite pleasing, changing the boric oxide content produced no marked effect.

A second burn was made at cone 02, in which the cooling was carefully regulated and the temperature held for $^3/_4$ hour at 1050°, 1000°, 950°, 900°, 850°, 800°, 750° and 700°C successively. Draw trials were taken at the end of each $^3/_4$-hour period, in order to determine the effect on the growth of crystals. The first crystallization showed up when the kiln had been allowed to cool to 950°C, and increased slowly with the decreasing temperature, but no trial piece drawn showed a greater degree of crystal growth than did the pieces of the first burn, cooled at the regular rate of the kiln (about 160° per hour for the first four hours).

There was no crazing in this series. In fact, the trial pieces drawn at high temperatures and cooled immediately did not show any such tendency.

Conclusions

The substitution of chromic oxide for iron oxide in a glaze of the type studied, even in amounts as small as .10 equivalent, decreases the fluidity to such an extent that crystal development is prevented entirely with low boric oxide content. With an increase in boric oxide, the fluidity is increased and hence the growth of crystals. Even with high boric oxide, however, the crystals are so minute as to be visible only on close examination.

Replacing the alumina by .10 equivalent chromic oxide likewise discourages the growth of crystals of such a size as to be readily visible.

Replacing the alumina by .05 equivalent of chromic oxide changes a high iron aventurine from an excessively crystallized rough matt to a glaze of high gloss with attractive and easily visible crystals. Although the addition of as low as .01–.02 equivalent of chromic oxide was not tried, the results would indicate that such an addition to a high iron aventurine would produce an excellent glaze.

The substitution of lithium oxide for sodium oxide does not promote an aventurine formation, but on the contrary is positively detrimental to its development. It does produce a micro-crystalline structure, and, in combination with chromic oxide, excellent matts.

High chromic oxide content results in crazing. High boric oxide and lithium oxide further encourage it.

Within the range of maturity of the glaze, no advantage is gained by burning to a higher temperature. A rapid oxidizing fire is desirable. Slow firing should be avoided, in order to prevent volatilization of boric oxide.

The best results were obtained in every case by allowing the kiln to cool without attempting to regulate it. It was impossible to observe any increase in crystal development from holding the temperature for two hours at 900°, 1000° or 1100°, nor could any change be noted when the temperature was held for $^3/_4$ hour at 1050°, 1000°, 950°, 900°, 850°, 800°, 750° and 700°C successively.

The writer wishes to express his appreciation for the interest and assistance of C. W. Parmelee, Director of Ceramic Engineering at the University of Illinois, at whose suggestion and under whose direction this work was done.

TERRA COTTA BODY INVESTIGATION[1]

By B. S. Radcliffe

Five clays were used in this investigation, namely: Indiana, Colchester, Lower Kittanning, Ohio, Kentucky and Goose Lake, Illinois. Our regular grog, and grogs made by calcining the above clays at cones 2–3 were mixed with the clays in order to produce practical terra cotta bodies.

Chemical analyses of four of the clays gave:

	Indiana clay	Ohio clay	Colchester clay	Goose Lake clay
Moisture	2.20	3.56	1.97	1.62
Ign. loss	7.05	6.45	6.74	7.61
SiO_2	60.87	58.63	60.38	57.82
Al_2O_3	23.67	25.09	25.33	27.42
Fe_2O_3	2.50	1.92	2.08	2.85
CaO	.70	.12	.19	Trace
MgO	.97	Trace	.67	.69
SO_3	.16	.30	.23	1.06
$KNaSO_4$	3.80	3.69	3.15	3.36

The grog and calcined clays were ground and sized and screen analyses made.

Screen Analysis

	Mesh							
	10	20	35	65	100	150	200	Fines
Regular grog	7.6	46.2	21.0	11.1	4.6	3.0	..	6.5
8–40	8.2	64.6	25.6	1.6	..	..	..	..
8–80	7.0	51.0	27.0	12.0	3.0	..	...	..
40–fines	8.0	..	8.0	29.7	20.7	9.5	17.4	14.7
Indiana clay								
Grog	2.5	39.2	26.0	14.4	5.5	...	3.6	8.8
8–40	2.5	64.0	33.5	..	..	..	..	..
8–80	2.5	43.0	32.5	17.5	4.5	..	..	..
40–fines	...	..	10.0	24.5	15.0	17.0	16.0	17.5
Colchester								
Grog	5.0	41.0	24.0	12.0	4.0	...	3.0	11.0
8–40	7.0	63.0	30	..	...	..	..	..
8–80	7.0	53.0	26.5	10.0	3.5	..	..	..
40–fines	...	..	10	20	20.0	16.5	13.0	20.5
Lower Kittanning								
Grog	2.5	32.5	28.0	16.5	5.5	...	4.0	10.5
8–40	4.0	53.0	43.0	..	..	..	..	..
8–80	4.0	36.5	34.5	20.0	5.0	..	..	..
40–fines	...	..	9.0	29.5	15.0	14.0	15.5	17.0
Kentucky								
Grog	5.0	36.0	25.0	15.0	5.0	4.0	..	10.0
8–40	6.0	63.0	31.0	..	..	..	..	..
8–80	6.0	44.5	28.5	17.0	4.0	..	...	..
40–fines	...	..	11.5	27.0	15.0	14.0	19.0	13.5

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[1] Presented at the Atlantic City Meeting, Feb., 1924 (Terra Cotta Division). Recd. Sept. 5, 1924.

Goose Lake	Mesh 10	20	35	65	100	150	200	Fines
Grog	6.0	43.0	25.5	12.0	4.0	..	3.0	6.5
8–40	7.0	61.0	32.0	..	..	..	..	..
8–80	7.0	46.0	28.5	15.0	3.5	..	..	..
40–fines	...	..	12.5	27.0	15.0	16.5	17.5	11.5

Eight bodies were made of each of the five clays, each body consisting of 60% clay and 40% grog. The first four of the series were made with the regular grog, and the second four with grog of a calcine of the clay in question. The grog sizes were in all cases, as ground: 8–80; 8–40; and 40–fines.

The body numbers were 361–368 inclusive for Indiana clay; 369–376 for Colchester; 377–384, Ohio; 385–392, Kentucky; 393–400, Illinois.

Five additional bodies were made with 100% of clay number respectively, 401–405 inclusive.

The bodies, using 40 lbs. of dry materials, were weighed out, mixed with the proper amount of water, tempered by running them through a small Mueller brick machine several times, and aged for about a week.

The Test Pieces.—The test pieces consisting of: ten 1″ x 1″ x 8″ bars for shrinkage, absorption and modulus of rupture tests: five 3″ x 3″ x 3″ cubes for cool-cracking tests; five $2^1/_2$″D x 5″ long cylinders with one rounded end for spalling tests were pressed from each body.

The test pieces were dried and burned, the drying shrinkage, burning shrinkage and total shrinkage data tabulated, modulus of rupture tests made and calculated, and quenching tests made. The quenching tests were made by heating sets of one piece from each body to a temperature of 400°C in five hours, holding them at this temperature for one hour and then dropping the pieces in ice water. Three sets were so tested and the tests repeated until practically all of the pieces cracked. A few bodies were not cracked after three quenchings and are tabulated as *not cracked*.

DATA ON FIRED TEST PIECES

BD	Per cent dry shrink.	Per cent burned shrink.	Per cent total shrink.	Absorption	Modulus of rupture	Number of quenchings
361	4½	2	6½	10.4	2250	1
2	4	2¾	7	10.6	2187	1
3	4	2½	6½	11.0	1980	1
4	5	2½	7½	9.3	3060	1
5	4½	2	6½	9.4	2889	1
6	4½	2	6½	9.3	2745	1
7	4½	2	6½	9.4	2295	1
8	4	2	6	9.5	3060	1
9	6	2½	8½	11.8	1809	3
370	5½	2	7½	11.2	1800	3
1	5	2	7	12.0	1719	3
2	5	2½	7½	10.0	2700	1

Data on Fired Test Pieces (*Continued*)

BD	Per cent dry shrink.	Per cent burned shrink.	Per cent total shrink.	Absorption	Modulus of rupture	Number of quenchings
3	5½	2¼	7¾	10.0	2007	1
4	5	2½	7½	11.0	1953	1
5	5½	2½	8	10.5	1638	not cracked
6	5	2½	7½	11.2	2520	1
7	4½	2½	7	11.4	1656	3
8	4½	2½	7	11.6	1773	not cracked
9	5	2	7	11.7	1593	3
380	5½	2½	8	10.7	2466	1
1	5	2	7	10.7	2268	1
2	4	2½	6½	10.4	2070	1
3	4½	2¼	6¾	10.6	1863	3
4	4	2½	6½	10.0	2673	1
5	4	2	6	10.7	1629	3
6	4	2¼	6¼	10.0	1845	1
7	4	2½	6½	11.0	1890	1
8	4	2¾	6¾	10.4	2340	1
9	4	2¾	6¾	9.5	2295	1
390	4	2½	6½	9.0	2313	1
1	4½	2	6½	10.0	1917	3
2	4	2½	6½	10.0	2340	1
3	5	2	7	11.3	1530	not cracked
4	5	2	7	10.5	1890	3
5	5	2¼	7¼	10.5	1620	not cracked
6	5	3	8	9.0	2295	1
7	5	2¾	7¾	9.7	2196	3
8	5	2½	7½	9.0	1953	3
9	5	2½	7½	9.7	1665	not cracked
400	5	2¾	7¾	9.0	2619	1
1	5½	4	9½	7.4	3060	1
2	7	5	12	8.4	3510	1
3	8	4	12	8.6	2925	1
4	5	4	9	7.7	2835	1
5	6½	5½	12	5.7	3060	1

Analysis of Data

1. Goose Lake clay is best in regard to cool-cracking. Ohio and Colchester clays are about equal in regard to cool-cracking and are second to Goose Lake. Kentucky clay is fourth. Indiana clay is the poorest of all.

2. No individual kind of grog appeared to deserve much preference. 8–40 mesh sized grog produces the best bodies in regard to cool-cracking. There is no choice between 8–80 and 8 to fines grog. 40 to fines produced the poorest bodies.

3. There is a rather clearly defined line between good and bad bodies in regard to cool-cracking in the modulus of rupture tests. Bodies with a modulus of rupture over 1800 do not withstand a good cool-cracking test.

Those with a modulus of rupture of 1800 or less do withstand a good cool-cracking test.

4. The chemical analyses indicate that the Al_2O_3 and SiO_2 content of a clay is quite important. The Goose Lake clay with 27.42 Al_2O_3 and 57.82 SiO_2 is much superior to any of the other clays and greatly superior to the Indiana clay with 23.67 Al_2O_3 and 60.87 SiO_2.

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Chicago, Illinois

Discussion

Secretary Clare: Mr. Radcliffe, to what do you attribute the fact that the Goose Lake clay withstood the cool-cracking tests best?

Mr. Radcliffe: We do not have a large amount of data on which to base an explanation but it seems that the alumina-silica ratio has quite an important bearing. With the higher alumina and lower silica we get away from that type of body and we know that the free silica changes from one type of quartz to the other at about 500–600°C.

Secretary Clare: You said that those bodies having the highest modulus of rupture showed the greatest tendency to cool crack. Is that general?

Mr. Radcliffe: Quite general.

Secretary Clare: Has that any correlation with the absorption at all?

Mr. Radcliffe: There was very little correlation. Those with the Goose Lake clay as grog had a lower absorption than those with the regular grog we used in the plant. The cool-cracking tests of all six of the bodies using Goose Lake clay were practically equal. However, the ones with the fine grog were poor in both cases, those with the regular grog or with calcined Goose Lake clay as grog stood practically the same test. Those with the Goose Lake grog had a lower absorption. However, I cannot correlate much between absorption and cool-cracking tests.

Secretary Clare: You say the bodies of highest modulus of rupture cool-cracked the most. Would that lead you to believe they were harder bodies?

Mr. Radcliffe: You would naturally conclude that, but this Goose Lake clay was the densest body.

Secretary Clare: Does that Goose Lake clay have any particular properties? Why did you pick that clay?

Mr. Radcliffe: We simply had that as a possible source of supply for our factory.

Secretary Clare: I would like to hear some discussion on the point that the elimination of all the fines makes a better body, for I would question that. There was some work done for glass pots where all the fines were eliminated making good glass pots. They had to have a portion of the fines just as a concrete mixture has to have a proportion of fine aggregate.

Mr. Radcliffe: My statement was that we could not discriminate between the 8–40 mesh grog and the 8–fine mesh grog, in regard to a body for cool-cracking. One stood as good as the other.

I would not recommend that kind of a body exactly for terra cotta because where you have this coarse grog it tends to give you a rough surface after the piece is dried. I simply gave the results as they came. The 8–40 and 8–fines were seemingly equally good as far as cool-cracking was concerned.

Mr. Minton: Why did you use an 8-mesh grog at all? It is customary to use a 16-mesh as coarsest in terra cotta.

Chairman Hottinger: That is our general practice.

Mr. Radcliffe: This is the size that we are using at the present time.

Secretary Clare: Eight-mesh?

Mr. Radcliffe: It all goes through an 8-mesh and there is some that just barely goes through.

Chairman Hottinger: I imagine there is a difference in the quality of the grog. All our grog is ground in a dry pan. If it goes through an 8-mesh, only a small portion of 8-mesh grog would be in there, the larger proportion would be very much finer than 8-mesh. Adding coarse grog to our body is a recent change to eliminate cool-cracking.

Mr. Radcliffe: We had some trouble with cool-cracking with between 20 and 25% of material that passed an 8-mesh screen. In order to get away from so much fines in our grog, we put in coarser screens. We have rotary screens. Three of them formerly screened to about 16-mesh and 2 screens gave coarser material. We took out the three that gave the fine and put in all coarse and that brought down our percentage of fine from between 20 and 25 to about 10 and 12. That unquestionably improved the resistance to cool-cracking.

E. C. Hill: In regard to Mr. Clare's question as to the relation between the transverse strength or absorption and the tendency to cool-crack, I might say that I have tested most of the terra cotta clays used in the east for cool-cracking, and have not found any relation between cool-cracking and absorption or transverse strength. Using the same grog, the tendency to cool-crack depends largely on the character of the clay used. A body made from Campbell's red clay and vitrified porcelain grog withstood the cool-cracking test better than our regular terra cotta body. The absorption of the red body was 5% and the terra cotta body 15%. I have found that some refractory sandy fire clays have a decided tendency to cool-crack.

In regard to the size of grog, I made some experiments a few years ago on cool-cracking which were reported in the *Journal*.[1] The results of these tests were similar to Mr. Radcliffe's in that fine grog (40–100 mesh) had a decided tendency to cool-crack, but with grog 16–40 mesh and 16–100 mesh there was not a great difference between them.

DR. LANGENBECK: It is always desirable, it seems to me, in taking tests of this kind to try to get something down to positive figures. The measurement of grog by the extremes of screens is not so accurate as it might be, because there are variations in the speed of machines, the pressure through bumping, etc., so it seems to me they will cause wide variations in the character of the grog apparently intended to be the same.

Suppose you have a certain kind of concrete work and you use pebbles and then different grades of sand? The purpose of the concrete maker, is to have a grade, a set of finer materials that will fill in the interstices between the pebbles and make possible a solid aggregate, so that each pebble or particle, down to the finest sand used, will be covered by a surface coating of cement which in setting binds the concrete together.

If you visualize for the moment in the concrete body that essentially (though with a larger layer of clay) the clay takes the effect of the water and the cement coating in the concrete aggregate. It seems to me that in making tests of this kind you should try to find the amount of interstitial space between the particles. The different grogs could be saturated with water; then put in a cylindrical graduate and the graduate filled with water to a definite volume. The volume of water added will give the actual interstitial space to be filled by the clay.

MR. RADCLIFFE: I did not try to grade the fines and the coarse to produce the densest grade or mixture of grogs as you suggested. I simply took the grogs and crushed them and got the various screen sizes that resulted from crushing.

MR. MINTON: I think Earl Montgomery made an exhaustive series of experiments about ten years ago on that line.[2] He has formulas which determine the exact quantity of the various sized grogs required to make a solid mass, exactly as Mr. Langenbeck has suggested. If you have a maximum sized grog to start with, this formula would give the sizes, roughly, within three or four different sizes that are required to fill up the voids between those.

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[1] "Experiments on Fire Cracking in Terra Cotta," *Bull. Amer. Ceram. Soc.*, **1** [10] 224; 226–29 (1922).

[2] *Trans. Amer. Ceram. Soc.*, **17**, 410 (1915).

Chairman Hottinger: Mr. Minton, did you ever use Montgomery's formula?

Mr. Minton: I was interested in dunting of sanitary ware. I found that the sizes of grog had something to do with dunting; that if we had a larger percentage of fine grog there was more of a tendency to dunt than there was when we kept out that large percentage.

In factory practice, unfortunately it is rather difficult to judge from day to day the various sizes of grog without actually screening them out. One day the grog is dry, the next day it is wet and it makes a tremendous difference in the various sized grains that you get when it goes through a crushing machine or dry pan or set of rolls. But as far as dunting is concerned, the question of free silica is far more important, perhaps, than the question of fineness of the grog.

Mr. Radcliffe referred to the proportion of alumina in silica. It seems to me his free and combined silica would have been even more indicative of that than the proportion of the total alumina to the total silica.

Mr. Radcliffe: The alumina is practically all combined with silica so that the amount of free silica in one case or the other would depend upon the per cent of each present in a clay.

Mr. Minton: I would not think so. Did you figure it out from your calculations—the amount of silica that is combined with the alumina?

Mr. Radcliffe: What I meant was if you have high alumina and low silica you have less free silica than if you have a low alumina and high silica. It does not give you the percentage but as far as this work was concerned, I believe the amount of free silica—just simply the chemical analysis would in this case be indicative of free or uncombined silica.

Mr. Minton: You are not dealing with clays that have a very high silica content. I used a clay silica content of 74%; there was quite a bit of free silica there and there would not be so much here, of course.

Mr. Radcliffe: There is considerable in this.

Chairman Hottinger: You do find a difference in the behaviors of clays as brought out by Mr. Radcliffe. With lower or higher silica we have extreme difficulties in dunting or fire cracking. When we strike a higher proportion of free silica we know that is detrimental to the ware.

As far as the action of the fine grog is concerned, we have nothing to base our facts on; no work has ever been done which will give anything accurate in the matter of what the action of fine grog will be. In years gone by I have made bodies with all fine grog and had no difficulty with them, but I do know from the analysis of the clays I used at that time that they were not very siliceous and consequently worked out very well.

Mr. Minton: Perhaps I should not make this statement, but I have found that terra cotta is very much easier to make than sanitary body when it comes to dunting.

Chairman Hottinger: Very much is dependent upon the kind of ware you are making and the total weight of the clay in the piece. The matter of shape also has something to do with it, and also certain stresses and strains where you have thin sections and thick sections. That would have to be taken into consideration.

E. C. Hill:[1] Mr. Radcliffe tested the various bodies in his investigation by heating test pieces in the form of cubes and quenching them in water. I think a more positive method would be to prepare pieces of considerable size similar to pieces generally manufactured, fire them in a test kiln and cool the kiln more rapidly than is done commercially. In making the tests in this manner, I have found some individual pieces that gave inconsistent results, so that it seems necessary to have several test pieces of the same body in order to arrive at definite conclusions. I should think that testing for cool-cracking by quenching would not give as consistent results as the method just mentioned.

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[1] Discussion submitted June, 1924.

ARTIFICIAL SILLIMANITE AS A REFRACTORY[1]

By Hewitt Wilson,[2] Clarence E. Sims,[3] and Frederic W. Schroeder[4]

ABSTRACT

Alumina-silica mixtures were prepared by fusing quartz, china clay, fire clay, and alumina in the electric furnace. When alumina is less than 68%, crystalline sillimanite ($3Al_2O_3 \cdot 2SiO_2$) with glass is produced. This material is not very resistant to loads at high temperatures because of the early fusion and internal lubricating action of the glass surrounding the crystals. Above 68% alumina, crystalline corundum appears and the glass is practically absent. This latter composition is very resistant to high-temperature loads when an interlocking, recrystallized bond is developed. This material is not affected materially by acid slags, but it cannot resist basic slags. However, the dense structure of a brick of material above 68% Al_2O_3 causes less slagging in a laboratory bath test than silica brick. The laboratory made sillimanite-corundum brick withstood higher temperatures than the best silica, magnesia, chrome, fire clay, or zirconia brick even though the cone of fusion of the former is less than that of MgO, Cr_2O_3 or ZrO_2. More and better service tests with a large number of brick fired in large kilns is needed to follow up this laboratory work.

Introduction

The possible use of sillimanite as a refractory material is of interest because of the limitations of the usual refractories, fire clay, silica and magnesia brick in the modern metallurgical processes. The more universal use of the electric furnace with its higher temperatures and rapid thermal changes has increased this interest. The inadequacy of the present refractory linings, resulting in a retarding in development of the open-hearth steel furnace, has caused a searching for a better refractory. Steel could be melted and purified faster if the furnace walls and roof would withstand high temperatures. Insulation cannot be used at the present temperatures on silica brick roofs. The capacity of open-hearth furnaces could probably be increased 35 to 40% and their thermal efficiency could probably be doubled if adequate refractories could be produced.[5]

Interest has been shown in sillimanite because of its high melting point, its definite chemical composition and crystalline structure which develops within reach of commercial temperatures. Crystalline materials have the ability to resist deformation to temperatures very close to their melting points. An unwarranted assumption that sillimanite should be chemically neutral at high temperatures has been made; but actual tests show that silica and alumina separated or combined in a definite chemical compound cannot resist the fluxing powers of lime, iron and other strong bases. Because of the use of natural forms of sillimanite in spark-plug porcelains, it is assumed that sillimanite refractories should be more resistant to thermal shock or spalling.

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[1] Published by permission of the Director, U. S. Bureau of Mines.

[2,3,4] Consulting Ceramist, U. S. Bureau of Mines, and Professor of Ceramics, University of Washington; Electrometallurgist, and Junior Chemist, respectively, Northwest Experiment Station, U. S. Bureau of Mines, at Seattle, Washington, in cooperation with College of Mines, University of Washington.

[5] Editorial on the limitation of open-hearth furnaces, *Fuels and Furnaces*, **1** [2], 63 (1923). C. E. Williams, "Requirements of Refractories for Electric Furnaces," *Jour. Amer. Ceram. Soc.*, **6**, 753 (1923).

Mineralogical and Chemical Properties

Natural Sillimanite.—Mineralogically, sillimanite is one of the andalusite group of minerals. The three members of this group are andalusite, sillimanite, and cyanite.[1]

PROPERTIES OF THE ANDALUSITE GROUP ($Al_2O_3 \cdot SiO_2$)

	Andalusite	Sillimanite	Cyanite
Crystalline system	Orthorhombic	Orthorhombic	Triclinic
Specific gravity	3.16–3.20	3.23–3.24	3.56–3.67
Hardness	7.5	6 to 7	7

Color. Variable for all: White to green, with gray, gray browns, and olive greens predominating.

Occurrence.—The three minerals are found in crystalline metamorphic rocks, such as feldspathic and cordierite gneiss, mica and paragonite schist, and are usually the result of contact metamorphism at low temperatures.

The three minerals consist of 62.9% by weight of alumina and 37.1% silica. They are unaffected by the common acids and bases and great difficulty has been found in dissolving them for chemical analysis by the ordinary alkali-fusion methods.

The 3:2 sillimanite ($3Al_2O_3 \cdot 2SiO_2$).—N. L. Bowen[2] and J. W. Greig[3] have discovered that the crystalline sillimanite formed in magmas, both natural and artificial, is not the monosilicate but a compound composed of three molecules of alumina and two of silica. The three minerals, andalusite, sillimanite, and cyanite, when heated to 1545°C will likewise change to the 3:2 ratio, and adopt a new crystalline form. Bowen and Greig have made the following changes in the binary system developed by Rankin and Wright:[4]

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[1] F. W. Clarke, "Data on Geo-Chemistry," U. S. Geol. Survey, *Bull.* **616,** 409 (1916).

[2] This work was completed before Bowen and Greig's discovery of $3Al_2O_3 \cdot 2SiO_2$ was known. Their discovery explained some of the phenomena encountered in this study and which were not explained by the alumina-silica diagram of Rankin and Wright.

$3Al_2O_3 \cdot 2SiO_2$ has been named mullite by Bowen. In this report it is called "3:2 sillimanite" to distinguish it from the natural low-temperature form, "$1\ Al_2O_3 \cdot 1SiO_2$."

[3] N. L. Bowen and J. W. Greig, "The System Al_2O_3–SiO_2," *Jour. Amer. Ceram. Soc.*, **7** [4], 238 (1924).

[4] G. A. Rankin and F. E. Wright, "The Ternary System CaO–Al_2O_3–SiO_2," *Amer. Jour. Sci.*, **39,** 9 (1915).

The eutectic has been changed from 13% alumina to 5.5% and its melting temperature from 1610°C to 1545°C. $3Al_2O_3 \cdot 2SiO_2$ (alumina, 71.8%, and silica, 28.2%, by weight) replaces the monosilicate at the high temperatures, but melts incongruently at 1810°C, the former eutectic temperature between the monosilicate and corundum. That is, corundum and liquid replaces $3Al_2O_3 \cdot 2SiO_2$ at 1810°C and the final traces of corundum disappear at 1930°C. As the incongruent melting temperature of $3Al_2O_3 \cdot 2SiO_2$ is practically the same as the melting temperature formerly given for the monosilicate (1816°C), no difference has been noted in the softening of sillimanite refractories from that expected, although, as will be shown later, it is necessary to increase the alumina content to near 70% before the silica glass can be eliminated.

Past Investigations of Sillimanite

Artificial crystalline sillimanite is a very common although a minor constituent of such ceramic bodies as porcelain, paving brick, pyrometric cones, glazes, glass pots, and many other aluminum silicates fired at high temperatures. It may be formed by heating amorphous materials in the sillimanite ratio to complete fusion; it appears in vitrified or partially fused clay bodies at intermediate temperatures and has been found in aluminous low temperature glazes and bodies which develop sufficient molten fluid for the formation of the crystals.

The growth of the sillimanite crystals has been given as the reason for a decrease in strength of certain refractory bodies on heating.[1] One of the causes of mattness of glazes is undoubtedly the crystalline development of sillimanite in the liquid magma on cooling,[2] for matt surfaces can be developed by mixtures of alumina and silica alone at high temperatures or at low temperatures if some molten liquid, such as lead oxide, is provided. Likewise, in glass tanks and pots, sillimanite will develop from the aluminous refractories in contact with the fluid glass.[3]

The first sillimanite brick were mixtures of bauxite or diaspore with impure fire clays approximating the monosilicate ratio. Such brick when hard fired have excelled the best of the fire-clay brick, but, nevertheless should not be called sillimanite brick, because they contain little of the crystallized compound. Grinding fire clay and diaspore in a dry pan does not bring the grains into a fine enough state of subdivision and intimate enough mixture and the usual fire-brick kiln heat develops but a small amount of crystalline sillimanite.[1]

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[1] J. W. Mellor, *Pottery Gazette*, 367 (1907); *Clay and Pottery Ind.*, 315; A. S. Watts, "A Possible Explanation of Failure under Load at High Temperatures as Displayed by Fire-Clay Refractories," *Jour. Amer. Ceram. Soc.*, **3,** 448 (1920); H. G. Schurecht, "Notes on the Effect of Firing Temperatures on the Strength of Fire-Clay and Stoneware Bodies," *Ibid.*, **4,** 366 (1921).

[2] A. S. Watts, "Crystalline Structure in Porcelains," *Trans. Amer. Ceram. Soc.*, **11,** 185 (1909). R. C. Purdy, "A Study of Glaze Composition on the Basis of Norms," *Ibid.*, **14,** 106 (1912); H. F. Staley, "Cost of Raw Lead Glazes," *Ibid.*, **19,** 669 (1917).

[3] N. L. Bowen, "The Identification of Stones in Glass," *Jour. Amer. Ceram. Soc.*, **1,** 596 (1918); G. V. Wilson and S. N. Jenkinson, *Jour. Soc. Glass Tech.*, **2** [5], 14 (1918); A. F. Gorton, "Observations of the Apparent Failure of Lead-Glass Pots," *Jour. Amer. Ceram. Soc.*, **1,** 655 (1918); S. English, "Natural Sillimanite as a Glass Refractory," *Jour. Soc. Glass Tech.*, **7,** 248, 258 (1923).

Noel Lecesne and A. Malinovszky have used an air-blast, coke-fired furnace to produce fusion of bauxites and fire clays, and while the fused products obtained show well developed sillimanite crystals, they are embedded in a ground mass of glass and consequently will not show rigidity under load at high temperatures.[2]

Present Investigation of Alumina-Silica Mixtures

The present investigation is a study of the refractory properties of electrically fused silica and alumina mixtures and includes fused quartz, fused fire clay, English china clay and mixtures of china clay and alumina.

The high temperature silica minerals (cristobalite and tridymite) crystallize very slowly from fusions of compositions between 100% silica and $3Al_2O_3 \cdot 2SiO_2$, hence these mixtures will contain silica glass. As the 3:2 sillimanite crystallizes very rapidly, crystalline $3Al_2O_3 \cdot 2SiO_2$ will be found in greater amounts as the alumina content is raised. From Bowen's diagram, mixtures containing more than about 55% alumina, if chilled suddenly from above 1810°C, will contain corundum and glass, but if cooled slowly through the fluid zone they will contain 3:2 sillimanite and silica glass when the alumina content is from 55 to 71.7%; and 3:2 sillimanite and corundum when the alumina is more than 71.7%. But very little glass will be present in the latter case (except as impurity) for corundum likewise crystallizes very rapidly.

Many different compositions will separate out in a large batch of silicate mixture melted in an electric furnace because of the lack of uniformity of the mix and the different rates of cooling in different parts of the mass. In this study, no batch was found which contained corundum and glass alone without some 3:2 sillimanite.

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[1] A. V. Bleininger, "Note on Load Behavior of Aluminous Refractories," *Jour. Amer. Ceram. Soc.*, **3,** 155 (1920).

[2] Noel Lecesne, "Manufacturing Refractory Materials with Fused Bauxite," *Trans. Ceram. Soc.* (Eng.), **17,** 192, and with A. Bigot, "The New Refractory and Abrasive Matter Called Corindite," *Ibid.*, **17,** 267 (1917–18); French Patent, 471,513, July 11, 1914, and English Patent, 17,289, 1916; A. Malinovszky, "The Malinite Process for the Production of Sillimanite Refractories," *Jour. Amer. Ceram. Soc.*, **3,** 40 (1920).

Preparation of the electrically fused materials.[1]

The electric furnace used for melting is shown in Fig. 1.

The fusion of these materials is difficult because its low electrical conductivity requires that the mass be heated almost to its fusion point before it becomes appreciably conductive.

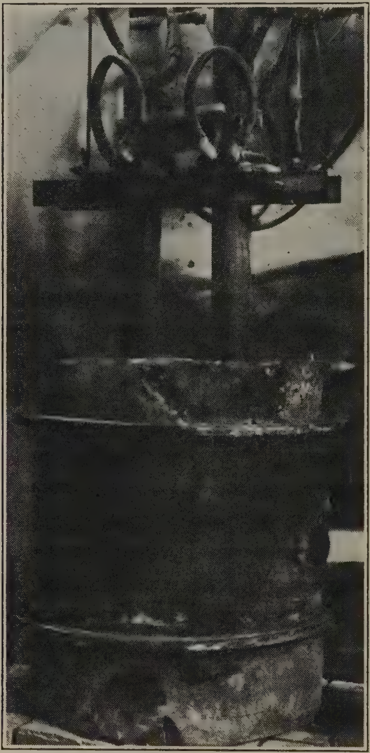

FIG. 1.—Furnace used in making sillimanite fusions.

Fine materials were agglomerated by mixing with water in a wet pan and forming into rough blocks. These blocks were dried and sometimes calcined. Calcining is preferable but not necessary. The blocks were broken to less than two inches and mixed with 5 to 10% sawdust.

The sawdust is used to facilitate the escape of evolved gases which otherwise would form miniature volcanoes and spatter fused and unfused material out of the furnace.

A layer of material from four to six inches deep was first placed in the bottom of the furnace. The electrodes were lowered until they rested upon this layer. A crushed carbon train was built between the electrodes and held in place by means of heavy paper wrapped around the electrodes. The shell was then filled.

A current giving a power input of from 40 to 60 kw.-hr. was maintained throughout the melt. At the start, due to the conductivity of the carbon, this power input was maintained with a potential between 30 and 50 volts. When the carbon had burned out making it necessary to arc through the partially fused charge, the potential had to be raised to over 100 volts. The electrical conductivity of the charge increased, however, with the temperature and the amount of liquid, hence the potential can gradually be lowered until at the end of the run it is approximately 60 to 70 volts.

The electrodes were withdrawn when the current was cut off.

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[1] The electric furnace procedure is covered in greater detail by a companion article, entitled "Preparation of Sillimanite for Refractory Uses," by C. E. Sims, H. Wilson, and H. C. Fisher, presented before the fall meeting of the American Electrochemical Society, 1924.

When cooled sufficiently to be solidified the shell was lifted from the fused block and the unfused material trimmed away.

A chart of a typical melt is given in Fig. 2.

Production of Sillimanite from Clay by Reduction of Silica Content

Sillimanite can be made by reducing the silica in clay. This is done by adding carbon to the charge. The silica removed is partially reduced to SiO. SiO is volatile at the temperature of reduction and escapes as a gas, burning at the surface of the charge to SiO_2 and forming dense white fumes. The remainder of the silica is reduced to silicon most of which, with iron, forms metallic globules of ferrosilicon containing a little aluminum. Because of this two-step reduction it is difficult to calculate the amount of carbon necessary for any required reduction, but the amount is readily determined with a few tests. The carbon starting train and electrodes reduce some silica even if no other carbon is present. The curve in Fig. 3 shows the decrease in silica content in a typical reducing fusion.

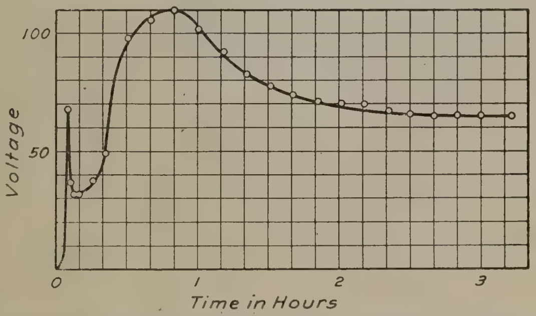

FIG. 2.—Curve showing the variation in voltage necessary to maintain a constant power input. This illustrates the variation in the resistance of the melt throughout the run.

Elimination of Ferrosilicon and Aluminum Carbide

Considerable trouble was experienced at first in the manufacture of brick from the electric-furnace fusions because of the presence of ferrosilicon, which oxidizes during the firing of the brick and ruptures the brick structure by its expansion. (See Fig. 4.)

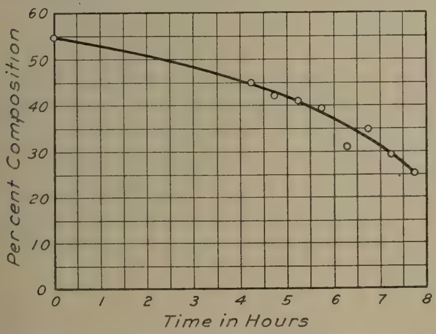

FIG. 3.—Curve showing the decrease in silica content of the fused portion of a charge during the melting and reduction of clay.

This ferrosilicon is formed by the reducing action of the carbon added and of graphite electrodes. When high in content of silicon and low in iron the ferrosilicon does not settle out of the fusion because its specific gravity is so near that of the molten sillimanite. Also, its shrinkage is very similar to that of the artificial sillimanite and the ferrosilicon globules closely adhere to the cooled melt. When the "pig" is broken, the ferrosilicon will fracture through the globule instead of away from the silicate. Being low in iron hence non-magnetic and insoluble in acids, its removal is very difficult. Ferrosilicon can be oxidized by roasting at low temperatures before the sillimanite is molded into brick but such treatment is expensive.

The only satisfactory means found for making possible the eliminating of ferrosilicon from the cooled melt is to add iron turnings to the charge, thus increasing Fe content of the ferrosilicon.[1] This will increase the specific gravity of the ferrosilicon (FeSi + Fe) and causes the globules to settle to the bottom of the molten bath. This also will increase its shrinkage thus forming loose pellets. If enough iron is added it becomes magnetic and then can be easily separated.[2]

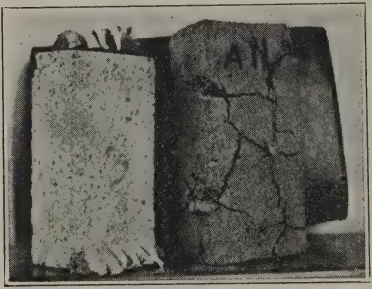

FIG. 4.—Right. Disintegration of sillimanite brick during firing by oxidation and expansion of ferrosilicon. Left. Calcined English china clay brick after two load tests to cones 23 and 26.

Methods of Testing

The control tests were chemical and petrographic analyses, cone fusion, and high-temperature load tests. The cone-fusion tests were made in a 5 by 5 by 5-inch oxygen-acetylene furnace[3] having an alundum or chromite lining. Cone 42 is easily reached. The high-temperature load test consisted of heating a standard-size brick, standing on end and subjected to a load of twenty-five pounds per square inch, to an increasing temperature until a 10% contraction, a failure by shearing, or the limit of the furnace was reached.[4]

Preparation of Sample Brick

The fused material, after the removal of the ferrosilicon and unmelted portions from the sides, was crushed to pass a 2-mesh sieve and that portion passing a 4-mesh was further reduced to pass 20-mesh. All magnetic parts were removed by an electromagnet.

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[1] EDITORIAL NOTE: The only Fe-Si compound positively known is FeSi. Fe_2Si is suspected but not proven. Solid solutions of FeSi and Fe are possible in all ratios. The larger the quantity of Fe dissolved with the FeSi, the more magnetic it will be.

[2] By the reducing influence of the electrodes, carbides of aluminum, calcium, etc., would be formed if all the SiO_2 and Fe_2O_3 in the mix was reduced to Si and Fe. Inasmuch as only enough carbon is added to bring the Al_2O_3-SiO_2 ratio from $^1/_2$ down to $^3/_2$ and to reduce the iron present or added, no carbides were formed or were possible in any of these sillimanite melts.

[3] Hewitt Wilson, "An Oxygen-Acetylene High-Temperature Furnace," *Jour. Amer. Ceram. Soc.*, **4** [10], 835–41 (1921).

[4] Hewitt Wilson, "High-Temperature Load and Fusion Tests of Fire Brick from the Pacific Northwest in Comparison with Other Well-known Fire Brick," *Jour. Amer. Ceram. Soc.*, **7** [1], 34–51 (1924).

The molding mixtures consisted of 50% 2- to 4-mesh, 40% minus 20-mesh, and 10% plastic material of the same composition as that used for melting. Gum arabic sorts of 0.2% was ground, dissolved in water, and mixed with the plastic portion before the latter was added to the melted material. The gum gave sufficient strength for dry handling and kiln setting. Eliminating the sizes between 4- and 20-mesh prevented elbowing of the coarse grains and gave approximately the densest and likewise a very strong structure.

The brick were molded by hand-tamping in a steel knock-down mold so arranged that the sides, ends, and bottom could be slid from the soft brick. For firing, the brick were placed on end on the center ring of the load-test kiln. The quick heating and cooling were very severe and it was expected that the results obtained would not be equal to those obtained in industrial kilns fired to the same temperatures for longer periods and cooled slowly.

Mixtures of Artificial Sillimanite and Glass. (Glassy Type.) Alumina Content from 0 to 68 per cent

Fused Versus Vitrified Silica-Alumina Mixtures Three melts were made of a local fire clay and one of the best grades of English china clay. The fused material was crushed and used with 5 and 10% of the original clay for standard-size brick, fired to cone 15. The vitrified fire-clay brick were made without grog; the vitrified china-clay brick were made with 90% English china-clay grog which had been calcined to a white vitreous body at cone 26. The molded china-clay brick were fired to cone 26. (See Fig. 4.)

Mixtures of English china clay and pure alumina were treated in the same manner, that is, calcining to cone 26 for the vitrified brick and fusing the mixture in the electric furnace for the fused sillimanite brick.

Results

Resistance to Load.—Table I shows that in resistance to load, the commercial silica brick in column 1 is superior to the amorphous materials which have been calcined to eliminate practically all the firing shrinkage, and also superior to the brick made of crystalline sillimanite, but containing glass, both in regard to the beginning of deformation and the final point of failure.

Item marked "load fusion" is the cone temperature at which shrinkage starts under twenty-five pounds per square inch and that temperature where 10% shrinkage is reached.

Silica glass, and fused fire clay containing large quantities of silica glass, or fusible silicates attained 10% shrinkage within two or three cones.

TABLE I

FUSED VERSUS VITRIFIED SILICA-ALUMINA MIXTURES

	SiO_2	95 plus	SiO_2	66	SiO_2	57	SiO_2	37
	Al_2O_3	2 (—)	Al_2O_3	34	Al_2O_3	43	Al_2O_3	63
	Cryst. silica brick	Fused[1] silica glass	Fire clay		English china clay		English china clay and alumina[2]	
			Vit.	Fused	Vit.	Fused	Vit.	Fused
Cone fusion	32–33	34–35	30–31	16–18	34	23	38	35–36
Load fusion	31	13–15	13–16	10–14	16–28	14–18	16–28	14–18
Type of failure	Shear	Slow yield	Slow yield	Shear	Slow yield	Shear	Slow yield	Shear
Load value[3]	10.62	2.8	3.19	1.75	7.58	4.57	7.17	4.94
Crystalline structure	Silica minerals	Silica glass	Glass	50% Sillimanite	Fine sillimanite in glass	Coarse sillimanite, 25% glass	Fine sillimanite in glass	Coarse sillimanite, small amount glass

[1] See Fig. 5.

[2] Only applicable to mixtures of 68% or less alumina. Melt No. 27 and 27-A.

[3] Hewitt Wilson, *loc. cit.*, **7** [1], 37 (1924).

English china clay and also English clay and alumina, gave a much slower yielding (from cones 16 to 28) when vitrified, than when fused. Even after a preliminary calcination to cone 26 shrinkage will commence as low as cone 16. With but two exceptions (starting at cone 19) all the commercial high aluminous and kaolin brick which have been tested in this laboratory (eight different brands) have started to shrink near cone 16 or before.[1]

Blocks of artificial sillimanite (containing excess silica) as removed from the electric furnace, in the shape of truncated pyramids, were subjected to a load of twenty-five pounds per square inch while the temperature was raised to over cone 32 in a period of seven hours. After cooling, the interior appearance and the dimensions of the block had not been changed, but the surface was covered with a glass about one-tenth of an inch in depth. The glass was very viscous and did not flow down the sides of the blocks even at the highest temperatures. This proved that a mass of interlocking sillimanite crystals even though individually coated with glassy sheaths has considerable resistance to load at high temperatures when the crystals form an interlocking skeleton with the glass as an internal phase. The glass acts as an external phase when a brick is molded of crushed crystalline fragments. (See Fig. 5.)

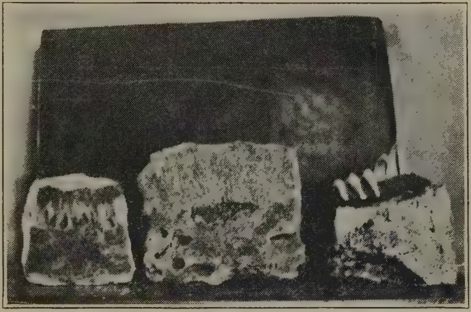

Fig. 5.—Left and middle. Broken blocks of crystalline artificial sillimanite taken from the electric furnace, after a load test to cone 32. Note the rigidity of the interior structure even though it contains blow holes. Right. Block of silica glass melted in the electric furnace, after a load test to cone 15. It softened at the same temperature as that of the sillimanite brick which contained glass.

Resistance to Fusion.—Having been previously fused, the cone of fusion or the high-temperature viscosity of the fire and china clays is reduced from 2 to 14 cones. The amount of reduction is greater with those clays of lower alumina and greater flux content.

Previous fusion produces a glass-like structure which is less rigid at high temperature than the vitrified structure of the calcined or vitrified materials.

Previous fusion converts quartz to silica glass and the other crystalline silicates to their corresponding glass forms, accompanied by a loss in density and rigidity at high temperatures.

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[1] Shearing is common if large grains of grog are imperfectly bonded with a plastic clay or if the bonding material softens before the grog particles. In the latter case the grog particles will be lubricated by the softened bond clay and will slide over each other in shear.

Slivers of artificial glassy sillimanite crystals consisting of one or more crystals, parallel with the length of the sliver, were broken from melt 27-A ($63Al_2O_3 \cdot 27SiO_2$) and heated with cones 34, 37, 38, 39 and 40. When withdrawn at cone 34, the point of the sliver was just beginning to glaze. At cone 37, the entire surface was glazed but the sliver was rigid. At cone 38, the sliver was greatly reduced in height but the central crystalline structure was still prominent. At cones 39 and 40, the rigid sliver had disappeared but the remaining mounds of glass were higher than the two Orton cones.

These crystals did not deform by curving like the standard Orton cones, amorphous fire clays, and incongruently melting feldspar crystals, but stood with a rigid core while the outer surface melted and flowed down the sides forming a puddle at the base, to which the center core was gradually reduced. If the temperature had been held at cone 37–38 or even lower, this same action would probably have taken place at a slower rate.

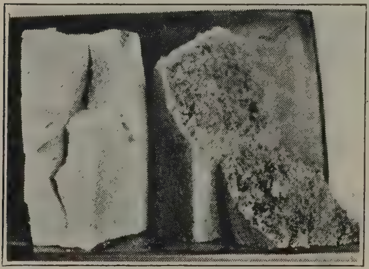


FIG. 6.—Right. Brick made of glassy type of artificial sillimanite after failure by shearing at cone 16 in high-temperature load test. Coarse-grained structure. Left. Glassy type of sillimanite which split through the center in the high-temperature load test due to imperfect recrystallization in the center.

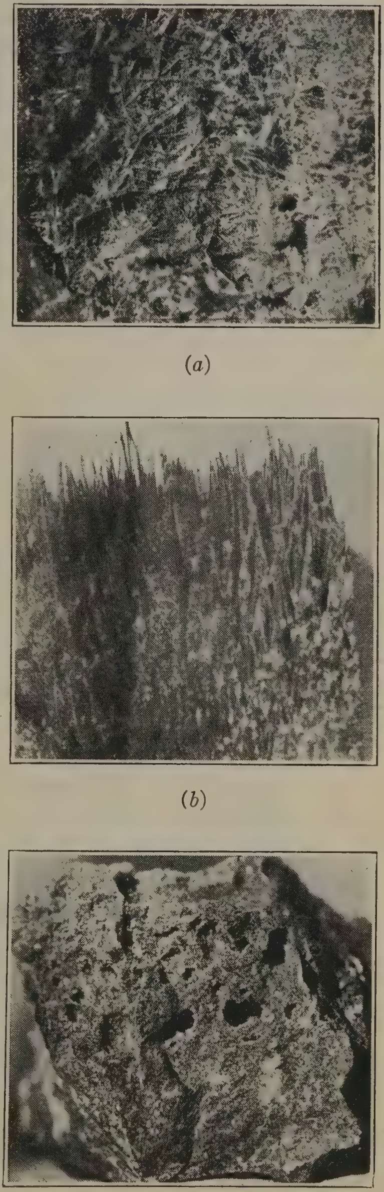
The action of the sillimanite crystals in the melt containing 63% alumina is apparently a case of the melting of an elongated crystalline structure preceded and hastened by the fusion and dissolving action of the accompanying glass. According to the Bowen-Greig diagram, when $3Al_2O_3 \cdot 2SiO_2$ is heated to 1810°C, it changes to a mixture of 36% corundum and 64% silicate glass (56% alumina and 44% silica). Unless very viscous, no cone could remain rigid with this quantity of fluid glass present and from the cone fusion indications sillimanite would have a definite melting point. Potash-feldspar crystals which melt incongruently by changing into leucite and silica glass soften throughout the mass so that the crystal bends and deforms in the usual cone fashion.

Cones made of the fused glass, chipped from the surface of the sillimanite block after it had been subjected to the high-temperature load test, deformed at cone 35–36 bending in the typical manner of amorphous materials. Cones made from samples of the entire melt ground to pass a 200-mesh sieve likewise deformed at cones 35–36 and show the high viscosity of the silica glass under very small loads.

Bonding Glassy Type of Artificial Sillimanite.—To avoid the production of more glass in the brick than was in the melt, it was thought advisable to keep the content of plastic bonding material as low as possible. Various mixtures were made from zero to 20% uncalcined English china clay and alumina. Good mechanical strengths were obtained by all when fired to cone 30. That is, enough of the glassy sheaths enveloping the crystals were fused together to provide a rigid glass bond at low temperatures, although the brick were rather brittle and had a tendency to crack in a fashion similar to the dunting of terra cotta and porcelain bodies.

None of these brick were able to resist the twenty-five pounds per square inch load above cone 18, and several sheared at cone 16.

Petrographic examinations showed that some recrystallization of artificial sillimanite developed between the crushed fragments from the outside toward the center and the difference was so pronounced in some brick that in the load test they split into two vertical halves. (See Fig. 6.) A firing to cone 33 over a period of twenty-four hours did not develop sufficient recrystallization to prevent the internal lubrication by the glass when subjected to load at high temperatures. The rigidity of the sillimanite block taken from the furnace melt was not reproduced.



(a)

(b)

(c)

Fig. 7.—The habits in which artificial sillimanite crystallizes.

(a) and (b) Sillimanite containing excess silica. (c) Sillimanite containing excess alumina.

Sillimanite-Corundum Mixtures (Stony Type)

Alumina Content above 68%

The preceding melts had an alumina-silica ratio of approximately 68 to 32. The crystals were large and well-developed, with shiny, glassy surfaces. The glass content, although small, was active enough to prevent good resistance to load at high temperatures.

Corundum appeared as another crystalline phase when the alumina content was raised to 70%. As it seems to crystallize out almost as rapidly as artificial sillimanite, mixtures between 71.7 and 100% alumina showed an interlocking structure of corundum and artificial sillimanite, with but traces of glass. The appearance of the melts changed from the coarse, glassy, well-formed crystalline structure to a dull, fine-textured mass Melts having the following ratios were made.

Melt number	Al_2O_3	SiO_2
28	70	30
29	76	22
52	88	12
54	85	15
61	90	7.8
67	95.5	1.5
68	68	31

Petrographic Analyses: Melt No. 29

The texture of this melt varied from rather dense to finely crystalline in appearance. In the vesicular portions, the blow holes were lined with corundum crystals. By examining crushed fragments it was found to consist chiefly of sillimanite with some corundum and a few minute metallic inclusions. A thin section showed short sillimanite crystals having the appearance of radiating from several centers and producing a fine-grained interlocking crystalline mass. Corundum crystals have replaced the glass. (See Figs. 7 and 8.)

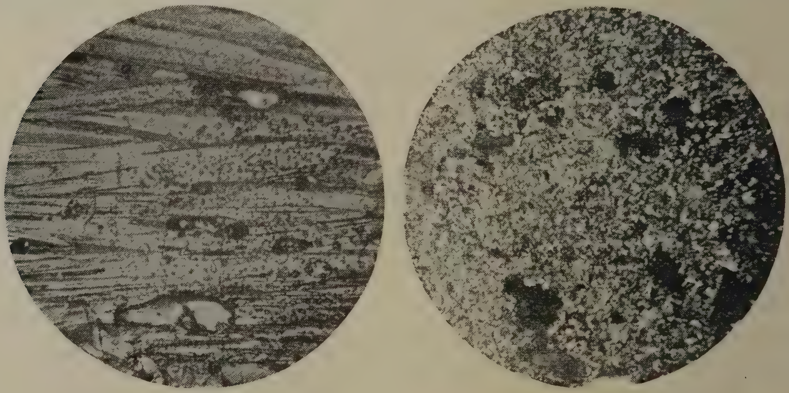

(*a*) (*b*)

FIG. 8.—Photomicrographs of thin sections of artificial sillimanite.

(*a*) Containing excess silica.
(*b*) Containing slight excess of alumina.

Melt No. 52 consisted of a "sugary" type of fine crystallization, composed chiefly of corundum.

Melt No. 54 also showed the fine crystallization but contained more sillimanite.

Load Test.—Brick made with 90% of each of the melts 28, 52 and 54 and 10% raw material were fired at various temperatures from cone 18–20 to over cone 33 and for various lengths of time. Very good load tests were obtained from all three melts if an interlocking crystallization had been effected and if the identity of the original crushed fragments had for the most part been lost. One brick made of melt No. 28, fired to cone 33 over a period of 18 hours, was subjected to three load tests at cones 28, 26, and 32 respectively. In each case, failure of the plungers which applied the load ended the test. The brick after these four heatings showed no shrinkage or signs of softening. Vertical cracks developed in the second test, but were only slightly enlarged in the third test. (See Fig. 9.) The interior of the brick was found to be very tough and strong, requiring considerable effort to break it.

The interior showed numerous circular cavities, which are probably water holes formed during molding. The majority of the original crushed fragments have lost their identities. Rupture occurred through the grains and not around them. Defective molding is probably responsible for the few unknit sections.

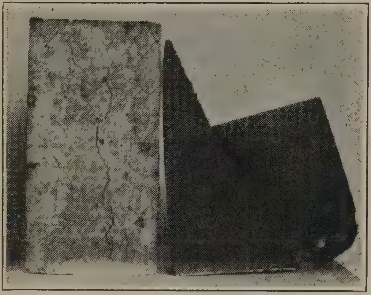


Fig. 9.—Left. Sillimanite-corundum brick of melt No. 28 after three high-temperature load tests between cones 26 and 32 without shrinkage. Right. Typical failure by shearing of the glassy type of artificial sillimanite plus silica.

Another brick of melt No. 28, fired to cones 18–20 over a period of forty-eight hours was entirely unaffected in the load test at cone 29. At this temperature the plunger failed and the test was discontinued. Cones 18–20 can be reached in well-designed combustion furnaces thus bringing the manufacture of these brick within the reach of well-known ceramic equipment and practices. The brick mentioned in these tests were all fired in the small 18-inch load test kiln. Cone 26 was brought down in at least eight hours and in cooling from the maximum temperatures, the furnace would be black in three to four hours. These severe conditions did not develop the best structure and this rapid rate of firing and cooling is itself a good test of the spalling properties of the brick.

(*To be continued*)

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ORIGINAL PAPERS

THE DEVELOPMENT OF SOME JEWELRY ENAMELS[1]

By H. G. WOLFRAM AND W. N. HARRISON

ABSTRACT

A series of thirty-three enamels having a constant melted portion of 20 silica, 30 lead oxide and 5 soda, and a variable melted portion of 45 parts was prepared and applied as powder to shallow cells in copper plates. Several of this field were used as fluxes in producing some transparent colored enamels.

Besides details of technique, the most important conclusions are: (*a*) all the better enamels contained boric acid plus lead or silica or both in the variable portion; (*b*) those having the highest ratio of lead oxide to silica were superior; (*c*) in those containing soda or potash, the latter seemed more desirable; (*d*) enamels ground to pass 80-mesh but retained on 100-mesh sieves produced the best results; (*e*) the color produced by a given stain was affected by the composition of the enamel; (*f*) the gloss, texture and general appearance of the enamel were affected by the coloring agent.

Introduction

Art enameling for ornamental purposes is perhaps the oldest form of man's attempt to apply glass or glaze to metals. Out of this early form of enameling practiced by the old Egyptian civilization has grown the present-day industry of enameling cast iron and steel, by methods which are fairly well understood, but the technique of enameling jewelry, medallions, and objects of a similar nature is not so well understood. The growing demand for this latter type of enameled ware has developed many unique and beautiful objects on the market of today.

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[1] Published by permission of the Director of the Bureau of Standards of the U. S. Department of Commerce. Presented at the Atlantic City Meeting, Feb., 1924 (Enamel Division). Received Oct. 11, 1924.

The Bureau of Standards has received numerous requests for information regarding the manufacture of jewelry enamels of the clear glass or cloisonné type and since the literature of the subject is so meager and generally devoid of specific information as to batch composition and technique of application, an investigation was undertaken at this Bureau in order to provide more information on this subject.

Review of Literature

Minneman[1] used, as a basis for his work, a formula for an enamel flux given in a publication by W. N. Brown[2] and although Brown gives this and several other formulas as typical of the trade, he adds that his treatise is general since compositions and processes of application of enamels are regarded as secrets by the trade and he recommends that the prepared enamels should be bought from dependable dealers.

Cunynghame,[3] Fisher,[4] and Maryon[5] in their respective writings state that jewelry enamels are essentially optical glasses of high lead content and gives several formulas for their preparation; nevertheless they also advocate that enamels should never be prepared by the enameler from the raw material, but should be purchased from some competent dealer.

Chapin,[6] Wethered,[7] Day[8] and Bowes,[9] write from artistic and historical points of view. The works are interesting but lacking in the details pertaining to composition and application. Bowes, however, gives several chemical analyses of Japanese enamels of the Middle Period.

Randau[10] treats the subject more from the standpoint of the manufacturer than any of the above authors, and gives several formulas and some general information on jewelry enamel, but the bulk of his work treats with enamels for iron and steel.

The enamels given in the references as yielding good results are limited to a relatively few types and are of widely different compositions as indicated in Table I.

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[1] Minneman, "Art Enameling on Metals," *Trans. Amer. Ceram. Soc.*, **13**, 514 (1911).

[2] Brown, "The Art of Enameling on Metal," Scott, Greenwood & Co., London.

[3] Cunynghame, "Art Enameling," and "European Enamels," A. Constable & Co., Ltd., and Methuen & Co., London.

[4] Fisher, "Enameling on Metal," The Studio, London.

[5] Maryon, "Metal Work and Enameling," Chapman & Hall, Ltd., London.

[6] Chapin, "How to Enamel Jewelry," J. Wiley & Son, New York.

[7] Wethered, "Mediaeval Craftsmanship and the Modern Amateur," Longmans, Green & Co.

[8] Day, "The Course of Art and Workmanship," B. T. Batsford, London.

[9] Bowes, "Japanese Enamels" (printed for private circulation).

[10] Randau, "Enamels and Enameling," Scott, Greenwood & Co., London.

TABLE I

MELTED COMPOSITIONS OF COLORLESS ENAMELS REPORTED AS GIVING GOOD RESULTS

Material	A[1]	B[2]	C[3]
Silica	25.50%	44.12%	55.70%
Lead oxide	71.42	35.70	38.20
Sodium oxide	3.08	4.08	6.10
Potassium oxide	...	7.03	...
Boric oxide	...	9.10	...

Preparation

Based on this table, thirty-three enamels were prepared, each of which consisted of a constant portion, in terms of melted weights, of fifty-five parts, namely: 20 silica, 30 lead oxide and 5 sodium oxide, and a variable portion, also in terms of melted weights, of forty-five parts. The forty-five parts of variable portion consisted of additions of oxides already contained in the constant portion or additions of other oxides which it was believed would contribute favorably to the appearance of the finished product. This gave a series or field of enamels which was divided into six distinct subdivisions, each representing a different percentage distribution of the variable constituents, an arrangement which facilitated a study of the effects produced by each component part. The batch compositions of the enamels are given in Table II, and the melted weights in Table III.

TABLE II

BATCH COMPOSITIONS OF JEWELRY ENAMELS (CALCULATED TO GIVE 100 PARTS MELTED)

No.	Silica parts	Red lead parts	Sodium nitrate parts	Potassium nitrate parts	Boric acid parts
1	35	46.1	54.8	....	....
2	35	46.1	13.7	32.2	....
3	35	46.1	13.7	....	26.6
4	35	30.8	54.8	32.2	....
5	35	30.8	54.8	....	26.6
6	35	30.8	13.7	32.2	26.6
7	20	46.1	54.8	32.2	....
8	20	46.1	54.8	....	26.6
9	20	46.1	13.7	32.2	26.6
10	20	30.8	54.8	32.2	26.6
11	50	46.1	13.7	....	....
12	50	30.8	54.8	....	....
13	50	30.8	13.7	32.2	....
14	50	30.8	13.7	....	26.6
15	20	61.5	54.8	....	....

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[1] Brown, *Loc. cit.*

[2] Commercial.

[3] Cunynghame, *Loc. cit.*

Table II (*Continued*)

No.	Silica parts	Red lead parts	Sodium nitrate parts	Potassium nitrate parts	Boric acid parts
16	20	61.5	13.7	32.2	....
17	20	61.5	13.7	....	26.6
18	50	38.4	34.3	....	....
19	50	38.4	13.7	16.1	....
20	50	38.4	13.7	....	13.3
21	50	30.8	34.3	16.1	....
22	50	30.8	34.3	....	13.3
23	50	30.8	13.7	16.1	13.3
24	20	61.5	34.3	....	....
25	20	61.5	34.3	16.1	....
26	20	61.5	13.7	....	13.3
27	40	46.1	41.1	....	....
28	40	46.1	13.7	21.5	....
29	40	46.1	13.7	....	17.7
30	30	61.5	27.4	....	....
31	30	61.5	13.7	10.7	....
32	30	61.5	13.7	....	8.86
33	42.5	53.7	13.7	....	....

Table III

Melted Weights of Jewelry Enamels

Constant portion 20 SiO_2, 30 PbO, 5Na_2O (parts); variable portion 45 (parts)

	Oxides					Rating of specimen with reference to			
No.	SiO_2 parts	PbO parts	Na_2O parts	K_2O parts	B_2O_3 parts	Bubbles	Attack on copper	General appearance	Final rating
1	35	45	20	..	..	1	2	1	4
2	35	45	5	15	..	2	2	3	7
3	35	45	5	..	15	4	4	4	12
4	35	30	20	15	..	1	2	2	5
5	35	30	20	..	15	3	3	3	9
6	35	30	5	15	15	2	4	4	10
7	20	45	20	15	..	4	2	2	8
8	20	45	20	..	15	3	4	4	11
9	20	45	5	15	15	4	4	4	12
10	20	30	20	15	15	1	1	1	3
11	50	45	5	..	..	1	3	2	6
12	50	30	20	..	..	1	1	1	3
13	50	30	5	15	..	2	2	2	6
14	50	30	5	..	15	2	4	4	10
15	20	60	20	..	..	3	2	2	7
16	20	60	5	15	..	3	2	2	7
17	20	60	5	..	15	4	4	4	12
18	50	37.5	12.5	..	..	2	3	3	8
19	50	37.5	5	7.5	..	2	3	3	8
20	50	37.5	5	..	7.5	4	2	3	9
21	50	30	12.5	7.5	..	3	2	2	7
22	50	30	12.5	..	7.5	2	4	4	10
23	50	30	5	7.5	7.5	2	3	3	8
24	20	60	12.5	7.5	..	4	2	1	7

25	20	60	12.5	..	7.5	1	2	2	5
26	20	60	5	7.5	7.5	4	3	2	9
27	40	45	15	..	..	1	2	2	5
28	40	45	5	10	..	1	3	3	7
29	40	45	5	..	10	2	3	3	8
30	30	60	10	..	..	1	2	2	5
31	30	60	5	5	..	3	3	3	9
32	30	60	5	..	5	4	4	4	12
33	42.5	52.5	5	..	..	3	2	2	7

The enamels prepared in batches of about 200 grams, were melted in crucibles in a small gas-fired crucible furnace and stirred when necessary to prevent segregation of the more refractory constituents during melting. The enamels which contained an excess of bubbles or portions of undissolved material were remelted. It was found that a single melt at a comparatively high temperature was more effective in producing a bubble-free enamel than repeated meltings at lower temperatures.

Usually molten enamels are poured into water to facilitate disintegration, but it was found that this procedure produced an undesirable amount of fine frit and, therefore, the enamels were cooled by pouring them onto a clean steel plate. They were then broken into small pieces and ground with a mortar and pestle to pass an 80-mesh sieve. The enamels prepared in this way, when applied to metal, contained an excess of fine bubbles which probably resulted from the rapid fusion of the fine particles over the surface making it difficult for the entrapped gas to escape, since the same enamel, from which the fines had been removed by rejecting the portions passing the 100-mesh sieve, produced much better results.

Although gold, silver and copper are commonly used as bases for jewelry enamels, copper only was used in this investigation because it is more easily obtained and it is known that enamels which work well on copper give equally good results on the noble metals, but the converse of this is not always true. One and one-half by two and one-half inch pieces of 18 gage sheet copper, in which shallow cells $^3/_4$-inch in diameter were made by stamping, were finally adopted as a satisfactory type of test plate after several trials were made with smaller cells. The plates were free from grease so the use of an alkaline cleaning solution was not necessary, but they were all pickled in hot dilute hydrochloric acid, rinsed in hot water and thoroughly dried previous to application of the enamel.

Application and Firing

It is customary in the application of opaque enamels to copper to use an organic bonding material to hold the enamel in place on the metal while it is being fired. The ordinary bonding materials are solutions of gum tragacanth, gum arabic or gum acacia, which are either mixed with the enamel or applied separately as a wash on the metal. It has been recommended that such solutions should be very dilute so that the organic material will completely burn out during firing. Although it is necessary to use a bonding material when the piece is fired in a vertical position or when enamel is applied to both sides of the ware, none was used in the application of the enamels here studied, because all specimens were fired in a horizontal position after filling the cells level full with the dry enamel.

The enamels were fired in an electric furnace at a temperature of about 950°C (1742°F) for one and one-half to two and one-half minutes, depending on the nature of the enamel and its thickness.

After firing, the enamel was ground down flush with the top of the cell, using carborundum as an abrasive, and then polished with a buffer using tin oxide and jeweler's rouge.

TABLE IV

RESULTS ON COLORED ENAMELS

Coloring agent	Per cent	Color	Base flux No. 3 Gloss	Texture	Remarks
Commercial black oxide	5.0	Black	Very good	Very few pinholes	Pinholes very small
Potassium dichromate	3.0	Dark green	Very good	Very good	Aventurine, finely distributed crystals
Copper nitrate	10.0	Yellowish green	Very good	Few pinholes	
Red iron oxide	10.0	Very dark brown	Very good	Wavy	
Black cobalt oxide	0.05	None	Very good	Very good	Color burned out oxide per cent too low
Black cobalt oxide	0.10	None	Very good	Very good	
Potassium permanganate	10.0	Reddish purple	Very good	Very good	Unevenly colored
Sodium uranate	7.5	Light amber	Very good	Very good	Attractive
Sodium uranate	15.0	Dark amber	Very good	Very good	Attractive

Coloring agent	Per cent	Color	Base flux No. 17 Gloss	Texture	Remarks
Commercial black oxide	3.0	Black	Good	Few pinholes	Attractive
Potassium dichromate	2.0	Dark moss green	Very good	Few pinholes	Dirty color
Green chrome oxide	1.0	Brownish green	Scummy	Many pinholes	Unevenly colored
Copper nitrate	15.0	Dark green	Very good	Few pinholes	Spotted with brown
Black copper oxide	5.0	Yellowish green	Scummy	Pinholes	Spotted with brown
Red iron oxide	5.0	Dark brown	Very good	Very good	Attractive
Black cobalt oxide	0.2	Very light blue	Very good	Very good	Attractive
Black cobalt oxide	0.25	Light blue	Not good	Wavy	Not good color

Potassium permanganate	15.0	Reddish purple	Very good	Very good	Attractive
Manganese dioxide	7.0	Dark reddish purple	Very good	Few pinholes	Unevenly colored

Coloring agent	Per cent	Color	Base flux No. 20		Remarks
			Gloss	Texture	
Commercial black oxide	3.0	Black	Scummy	Very good	Very attractive
Potassium dichromate	2.0	Pea green	Very good	Very good	Very attractive
Green chrome oxide	1.0	Pea green	Very good	Very good	Very attractive
Copper nitrate	15.0	Dark brownish green	Good	Few pinholes	Not good color
Black copper oxide	5.0	Dark brown	Very good	Very few pinholes	Not good color
Red iron oxide	5.0	Mahogany	Very good	Spotted	Very attractive
Black cobalt oxide	0.25	Dark seal brown	Very good	Few pinholes	Not good color
Black cobalt oxide	0.30	Mixture of blue and brown	Good	Good	Not good color
Potassium permanganate	15.0	Light brown	Very good	Very good	Attractive
Manganese dioxide	7.0	Brown	Very good	Very good	Attractive
Sodium uranate	7.5	Light amber	Very good	Very good	Very attractive

Coloring agent	Per cent	Color	Base flux No. 29		Remarks
			Gloss	Texture	
Commercial black oxide	3.0	Black	Good	Pinholes	Attractive
Potassium dichromate	2.0	Moss green	Very good	Few pinholes	Attractive
Green chrome oxide	1.0	Moss green	Very good	Vew few pinholes	Attractive
Copper nitrate	15.0	Dirty green	Very good	Very few pinholes	Not good color
Black copper oxide	5.0	Dirty green	Good	Very few pinholes	Not good color
Red iron oxide	5.0	Mahogany	Very good	Very good	Very attractive
Black cobalt oxide	0.25	Very light blue	Good	Few pinholes	Very attractive
Black cobalt oxide	0.30	Very light blue	Good	Few pinholes	Very attractive
Potassium permanganate	15.0	Dark reddish purple	Very good	Few pinholes	Attractive unevenly colored
Manganese dioxide	7.0	Light reddish purple	Very good	Very good	Very attractive
Sodium uranate	7.5	Light amber	Very good	Very good	Very attractive

TABLE IV (*Continued*)

Coloring agent	Per cent	Color	Base flux No. 6 Gloss	Texture	Remarks
Commercial black oxide	3.0	Black	Very good	Very good	Attractive
Potassium dichromate	2.0	Moss green	Very good	Few pinholes	Attractive
Green chrome oxide	1.0	Moss green	Very good	Few pinholes	Attractive
Copper nitrate	15.0	Dark green	Very good	Very good	Spotted with brown
Black copper oxide	5.0	Dark green	Very good	Very good	Spotted with brown
Red iron oxide	5.0	Orange red	Very good	Few pinholes	Unevenly colored
Black cobalt oxide	0.25	Light blue	Very good	Good	Very attractive
Black cobalt oxide	0.30	Dark blue	Very good	Very good	Very attractive
Potassium permanganate	15.0	Brownish black	Very good	Few pinholes	Very hard to burn
Manganese dioxide	7.0	Reddish purple	Very good	Very good	Unevenly colored
Sodium uranate	7.5	Light yellow	Very good	Few pinholes	Attractive

Coloring agent	Per cent	Color	Base flux No. 14 Gloss	Texture	Remarks
Commercial black oxide	3.0	Black	Good	Pinholes	Attractive
Potassium dichromate	2.0	Moss green	Very good	Very good	Very attractive
Green chrome oxide	1.0	Moss green	Very good	Very good	Very attractive
Copper nitrate	15.0	Dirty brown	Scummy	Pinholes	Not good
Black copper oxide	5.0	Dirty brown	Scummy	Pinholes	Not good
Red iron oxide	5.0	Brown	Scummy	Pinholes	Not good
Black cobalt oxide	0.25	Very light blue	Very good	Few pinholes	Attractive
Black cobalt oxide	0.30	Light blue	Very good	Few pinholes	Very attractive
Potassium permanganate	15.0	Dark brown	Scummy	Pinholes	Not good
Manganese dioxide	7.0	Reddish purple	Very good	Very good	Unevenly colored
Sodium uranate	7.5	Light amber	Very good	Very good	Attractive

Coloring agent	Per cent	Color	Base flux No. 32 Gloss	Texture	Remarks
Commercial black oxide	3.0	Black	Very good	Very good	Very attractive
Potassium dichromate	2.0	Dark green	Very good	Very good	Very attractive

Green chrome oxide	1.0	Dark green	Very good	Very good	Very attractive
Copper nitrate	15.0	Brownish green	Very good	Very good	Somewhat spotted
Copper oxide	5.0	Brownish green	Very good	Very good	Somewhat spotted
Red iron oxide	5.0	Reddish brown	Very good	Very good	Very attractive
Black cobalt oxide	0.25	Light blue	Very good	Very good	Very attractive
Black cobalt oxide	0.30	Light blue	Very good	Very good	Very attractive
Potassium permanganate	15.0	Wine color	Very good	Very good	Very attractive
Black manganese oxide	7.0	Light brown	Very good	Very good	Very attractive
Sodium uranate	7.5	Light yellow	Very good	Very good	Very attractive

Colored Enamels The colored enamels were prepared by taking as base fluxes colorless enamels Nos. 3, 6, 14, 17, 20, 29 and 32 (Table III) which represent a rather wide range in composition and at the same time include some of the best colorless enamels obtained. The preparation, application and firing were the same as for the colorless type except that a stain in the form of metallic salts or oxides was added to the raw batch before melting. The percentage of coloring ingredient used and the results obtained are given in Table IV.

Results

Colorless Enamels The effects of the different variable constituents upon the properties of the fired specimens are shown in Table III. The finished specimens were rated numerically according to: (*a*) general appearance, (*b*) freedom from bubbles, and (*c*) freedom from attack on the copper, since these were the chief factors affecting the quality of the enamel. The best were rated at four and the poorest at one. The most satisfactory enamel, then, has a rating of twelve found in the column headed, "Final Rating."

The relative desirability of various ratios of lead oxide and silica both to each other and to the other variable constituents, can be seen by comparing the several groups of enamels, considering as a group all the enamels in which the ratio of lead oxide to silica is constant. As the data in Table III show, the enamels containing only lead oxide and silica in the variable portion (Nos. 11 and 33) were not very satisfactory. However, all the satisfactory enamels include one or both of these constituents in the variable portion and the only enamel which does not contain either (No. 10) is one of the two least promising included in this study.

Concerning the enamels which did contain silica or lead oxide or both in the variable portion, it was observed that: (*a*) the four groups consisting of enamels Nos. 7, 8, 9; 30, 31, 32; 15, 16, 17; and 1, 2, 3 (Table III) produced the best results and are among those in which the ratio of lead oxide to silica is the highest; (*b*) the three groups consisting of Nos. 21, 22, 23; 4, 5, 6; and 12, 13, 14 produced some good enamels; (*c*) the two groups consisting of Nos. 18, 19, 20; and 24, 25, 26 show less variation in quality as the constituents are substituted one for another and the enamels of these groups are only fair; (*d*) the group consisting of enamels Nos. 27, 28, 29 does not contain any very satisfactory enamel. No. 29 was the best of this set.

The relative effects of soda, potash and boric acid upon the qualities of the fired specimens can be seen by comparing the enamels in the groups having constant lead oxide-silica ratios. Such comparison shows there is a decided tendency for progressive improvement in the elimination of bubbles and the reduction of attack on the copper as potash was substituted for soda and boric acid in turn for potash. All the satisfactory enamels contained boric acid, which seemed to eliminate attack on the copper. This does not agree with the results obtained by some investigators of white enamels for copper, but their compositions vary considerably from the enamels studied in this work in that the white enamels contained opacifying materials. It is interesting to note, however, that the silica and lead oxide contents of the white enamels are within the limits indicated as satisfactory for the clear glass type of this investigation. Furthermore, the boric acid content of the above-mentioned white enamels is low, from which it may be concluded that other constituents were responsible for the attack on the copper. From these results it appears that the best enamels are obtained by substituting potash for soda, by the addition of boric acid and by increasing the lead content. The best colorless enamels obtained were Nos. 9, 32, 17, and 3 (Table III) and the next best were Nos. 8, 6, 14 and 22.

Colored Enamels As previously stated, the colored enamels were produced by adding metallic salts or oxides as the stain to a base of colorless enamel. Base enamels Nos. 3 and 17 (Table III) were chosen for the first work because of their superior qualities as colorless enamels. From the experience gained with these two, some new coloring agents were used and the per cent of others changed in subsequent experiments with colors as shown in Table IV.

In studying the results given in Table IV, it is evident that the composition of the enamel is an important factor in the production of satisfactory colors, for not only was the color produced by a given stain affected by the composition of the enamel used, but the coloring agents affected the gloss, texture and general appearance of the enamel.

It was noted in practically all cases where copper nitrate was used as the coloring stain that the time required for firing affected the shade of color produced. This variation can probably be attributed to the changing states of oxidation of the copper in the enamel. There seemed to be practically no difference in the results obtained when chromium oxide was substituted for potassium dichromate or copper oxide for copper nitrate when this substitution was made giving equal amounts of the oxides in the melted enamel.

Conclusions

The following conclusions have been reached from the results obtained in this work:

1. Melting the enamel at a temperature high enough to produce a very fluid melt most effectively eliminated bubbles. In the case of highly refractory or viscous enamels remelting was beneficial.
2. Enamels ground to pass 80-mesh but retained on the 100-mesh sieve produced the best results on the fired specimens.
3. All the successful enamels contained boric acid with silica or lead oxide or both in the variable portion.
4. The best enamels were among those having the highest ratios of lead to silica.
5. In the enamels containing soda or potash, the latter seemed to be the more satisfactory.
6. The color produced by a given stain was affected by the composition of the enamel used.
7. The gloss, texture and general appearance of the enamel were affected by the coloring agent.
8. The oxides of chromium and copper may be substituted for the salts of these metals as stains without changing results.

COLORS IN A ZINC SILICATE GLAZE[1]

By Hobart M. Kraner

ABSTRACT

This represents a study of the effects of the seven common coloring oxides when introduced in a typical zinc silicate or willemite crystalline glaze. All the possible two- and three-color combinations for each colorant with a moderate color concentration and another similar series for strong color concentrations were investigated.

A new method by which fritting the glaze is obviated through the use of sodium silicate is described. The soluble sodium content is introduced by sodium silicate rather than by a frit.

Color absorption by the crystal was found to be most pronounced in the case of cobalt, decreasing in order with copper, manganese, iron, nickel, uranium and little, if any, absorption of chromium.

Description of color effects of most of these would be inadequate.

Introduction

In the literature of previous work considerable data are available giving formulas and firing behavior of the most practical and most easily produced crystalline glaze type, the zinc silicate or willemite glaze. Only scattered information is available, however, to show how the more interesting color effects may be obtained without a great deal of preliminary experimental work. This is to be regretted for the reason that the possible use of crystalline glazes in the decorative arts, such as that for which faience tile is being used, is extensive due to the rich textures obtainable.

In most cases where color has been used in such glazes, the color chosen seems to have been cobalt. From the results of this present study, it is somewhat obvious that this is probably due to the high luster of the glaze when this colorant is used and the completeness with which it is absorbed by the crystal, leaving a background glass of a different and contrasting color.

Clement[2] described his color study in zinc silicate glazes in which he obtained celadon green with CuO, blue with CoO, yellow-red with chromium, and Persian blue with blue crystals when nickel was used.

In Stull's[3] work some of the common coloring oxides were used, these being added to the glaze formula up to .05 equivalents. CoO, CuO, MnO, FeO were found to give pleasing effects. Chromium retarded or prevented crystallization.

Riddle[4] added 0.6% CuO to his glazes and obtained a turquoise blue, but this color, with copper, was probably produced by the influence of the RO constituents. He found MnO and FeO equally interesting.

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[1] Presented at the Atlantic City Meeting, Feb., 1924 (Art Division). Received Oct. 4, 1924.

[2] Clement, *Trans. Amer. Ceram. Soc.*, **4,** 38 (1902).

[3] Stull, *Trans. Amer. Ceram. Soc.*, **6,** 191 (1904)

[4] Riddle, *Trans. Amer. Ceram. Soc.*, **8,** 336 (1906).

Pukall[1] used a number of different coloring oxides including those of some of the rare metals such as tungsten, molybdenum and vanadium. Of the more common oxides he says, "colors may be chosen to suit except chromium."

The glazes described by Taxile Doat[2] are of the willemite type in which colors are derived from CoO, Fe_2O_3, and Fe_2O_3 contained in the rutile used. When he used chemically pure TiO_2 he obtained white crystals in many cases.

From the writer's experience it would seem that the fritting of the glaze is the most objectionable feature, inasmuch as it retards the production of these glazes by the artist or amateur who has only a small equipment available, rather than improper control of the firing and cooling involved. From a commercial standpoint this is also true in addition to the troubles attendant upon the use of a glaze which is 100% frit, and which must be applied through the use of gums or molasses. The application and firing problems are also multiplied inasmuch as during the heating-up period the gum is oxidized and the frail glaze powder often drops from the ware leaving bare spots which are not healed in many cases by the subsequent flowing of the glaze.

The process about to be described, although it has its objectionable features, may be used to advantage either by the amateur, or in the factory with a much greater certainty of the pieces coming through with no bare spots, resulting from glaze dropping from the ware during firing.

A 47° Baumé sodium silicate containing:

Na_2O	13.7%
SiO_2	32.9%
H_2O	53.4%

is not appreciably absorbed by a piece of whiteware or faience biscuit having as much as 10% absorption. The molecular formula of such a silicate is:

1.0 Na_2O 2.49 SiO_2 13.54 H_2O Molecular weight 455.1

This may be used as a source of Na_2O and SiO_2 in a glaze of the willemite type without affecting the fusion properties of the glaze.

The glaze may be made in a mortar, in a paint mill or in a ball mill equally well, and grinding does not seem to be necessary for good results. A smooth consistency is all that is necessary for proper application. This may be done by dipping the piece in the glaze or by painting the glaze onto the piece with a brush. After the glaze has dried on the piece it is hard and tough similar to a very thick coating of varnish. It can, therefore, be handled roughly without any danger of chipping or rubbing any of the glaze from the piece. In the case of tile, the thoroughly dried glazed pieces may be stacked one on top of the other without any danger to the glaze coating.

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[1] Pukall, *Trans. Amer. Ceram. Soc.*, **10,** 183 (1908).

[2] "Grand Feu Ceramics," 1905, Ceramic Studio Pub. Co., Syracuse, N. Y.

During firing the water expelled from the silicate causes the surface to be raised somewhat but after this has been expelled, the glaze coat soon settles back into place with no loss of material from the surface.

Such a means of preparation, although theoretically not as thorough in molecular distribution and approach toward chemical equilibrium as in fritting, is nevertheless better than addition of a flux or RO constituent to a raw glaze by way of a granular material.

Procedure

Preliminary work indicated that the base glaze:

$$\left.\begin{matrix} 0.33\ Na_2O \\ 0.67\ ZnO \end{matrix}\right\} \begin{matrix} 1.8\ SiO_2 \\ 0.3\ TiO_2 \end{matrix}$$

was very satisfactory with the coloring oxides whether they were added before or after fritting. It also proved satisfactory with the Na_2O added as sodium silicate. This formula is similar to the Sprechsaal glaze described by Stull[1] and is also covered in the work of Purdy and Krehbiel.[2]

The batch weight of this glaze using the above-described sodium silicate as a source of Na_2O and some of the SiO_2 becomes:

Sodium silicate	150.18	TiO_2	24.00
Flint	58.80	H_2O	15.00[3]
ZnO	54.27		

The colors were added to the above glaze rather than substituted for another RO in the molecular formula. The glaze and color were prepared by milling together for two hours in one gallon laboratory ball mills. They were blended by weight and applied to bisqued faience tiles or biscuit vases with either one or two applications. The latter is most advisable in the case of a vase having somewhat straight sides down which some of the glaze would flow during firing and in which thin glaze coat crystallization is usually retarded.

The same firing behavior as pointed out by most other workers was observed, except that it might be mentioned a somewhat rapid increase in temperature carrying all of the glaze ingredients into solution before the mass has had an opportunity to flow from the piece. This seems to be more important for prolific crystal development than close control of the cooling, and seems to be true for fritted glazes as well as for the sodium silicate glazes.

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[1] Stull, Discussion, *Trans. Amer. Ceram. Soc.*, **4**, 38 (1902).

[2] Purdy and Krehbiel, *Trans. Amer. Ceram. Soc.*, **9**, 319 (1907).

[3] This is enough to make a good consistency for grinding and application. A larger amount makes the glaze thin and would probably permit absorption of silicate by the porous body of the ware.

Figure 1 shows firing curves which produced good crystallization in a laboratory kiln fired with gas to cone 7 down, under oxidizing conditions. The tiles were passed through the 93-foot tunnel kiln to cone 9 half down[1] in seventeen hours. In the continuous kiln the tiles were laid flat upon the car top and were exposed to the direct action of the gases through the entire length of the kiln. Oxidizing conditions (4% O_2) prevailed.

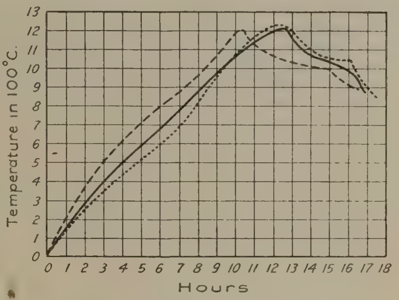

FIG. 1.

The following molecular equivalents of single coloring oxides were added to the glaze with the results indicated.

ONE COLOR SERIES

	Molecular equivalents of color added							Four concentrations of each color	
No.	CoO	MnO	CuO	UO_3	NiO	FeO	Cr_2O_3	Crystal	Background
1	0.01							Pale	Creamy
2	.025							Normal blue	Creamy
3	.05							Dark blue	Buff
4	.10							Dark blue	Brown
5		0.01						Fawn	Buff
6		.025						Fawn	Buff
7		.05						Fawn	Brown
8		.10						Dark fawn	Dark brown
9			.01					Very pale green	Pink and cream
10			.025					Delicate pale green	Pink and cream
11			.05					Normal copper green	Pink to tan
12			.10					Dark green	Brown taupe
13				0.01				White or yellow tint	Pale yellow
14				.025				Colorless to creamy	Creamy
15				.05				Pale yellow	Yellow
16				0.10				Pale yellow	Yellow
17					0.01			Pale bluish green	Yellow
18					.025			Pale bluish green	Apple green
19					.05			Apple green	Apple green
20					.10			Few green crystals	Shiny clear green
21						0.01		Colorless	Yellow
22						.025		Colorless	Yellow or buff

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[1] See Fig. 2 and *Jour. Amer. Ceram. Soc.*, 5 [6], 267 (1922).

TABLE (*Continued*)

	ONE COLOR SERIES Molecular equivalents of color added		Four concentrations of each color	
No.	FeO	Cr_2O_3	Crystal	Background
23	.05		Buff	Brown and buff
24	.10		Buff	Brown
25		0.01	No crystals	Shiny clear green
26		.025	No crystals	Shiny clear green
27		.05	No crystals	Shiny clear green
28		.10	No crystals	Shiny clear green

Using members 2, 6, 10, 14, 18, 22, 26 containing moderate color concentrations, the following mixtures and results were obtained:

	TWO COLOR BLENDS Molecular equivalents of color added							Moderate color concentrations	
Blend	CoO	MnO	CuO	UO_3	NiO	FeO	Cr_2O_3	Crystal	Background
2–6	0.012	0.012						Dark blue	Brown
2–10	.012		0.012					Pale blue	Light brown
2–14	.012			0.012				Moderate blue	Creamy
2–18	.012				0.012			Light blue	Yellow
2–22	.012					0.012		Light blue	Light brown or tan
2–26							0.012	No crystals	Shiny clear green
6–10		.012	.012					Pale green	Fawn to pink
6–14		.012		.012				Cream	Fawn to buff
6–18		.012			.012			Bluish green	Cream
6–22		.012				.012		Creamy	Fawn
6–26		.012					.012	No crystals	Bright green
10–14			.012	.012				Pale green	Pink or creamy
10–18			.012		.012			Pale green	Pink
10–22			.012			.012		Pale green	Creamy or fawn
10–26			.012				.012	Mossy, no crystals	Mottled, reddish brown
14–18				.012	.012			Pale greenish yellow	Yellow
14–22				.012		.012		Colorless to creamy	Light yellow
14–26				.012			.012	No crystals	Bright green
18–22					.012	.012		Pale bluish green	Pink to cream
18–26					.012		.012	No crystals, mossy	Shiny apple green
22–26						.012	.012	No crystals	Brownish green

Using members 2, 6, 10, 14, 18, 22 and 26, the following three-color combinations were blended:

	Molecular equivalents of color added							Moderate color concentrations	
Blends	CoO	MnO	CuO	UO_3	NiO	FeO	Cr_2O_3	Crystal	Background
2–6–10	0.008	0.008	0.008					Pale blue	Light buff
2–6–14	.008	.008		0.008				Moderate blue	Buff
2–6–18	.008	.008			0.008			Pale blue	Yellow
2–6–22	.008	.008				0.008		Pale blue	Cream
2–6–26	.008	.008					0.008	Green	Brown
2–10–14	.008		.008	.008				Pale blue	Greenish brown
2–10–18	.008		.008		.008			Pale blue	Pink to creamy
2–10–22	.008		.008			.008		Moderate blue	Buff
2–10–26	.008		.008				.008	Mossy bluish gray	Greenish brown
2–14–18	.008			.008	.008			Pale blue	Yellow
2–14–22	.008			.008		.008		Pale blue	Yellow
2–14–26	.008			.008			.008	Dark green	Shiny apple green
2–18–22	.008				.008	.008		Light blue	Pale yellow
2–18–26	.008				.008		.008	None	Shiny brownish green
2–22–26	.008					.008	.008	None	Bright dark green
6–10–14		.008	.008	.008				Pale green	Pink to brown or buff
6–10–18		.008	.008		.008			Pale green	Pink or buff
6–10–22		.008	.008			.008		Pale green	Pink or buff
6–10–26		.008	.008				.008	Mossy brown	Reddish brown
6–14–18		.008		.008	.008			Pale green	Yellow
6–14–22		.008		.008		.008		Colorless	Creamy yellow
6–14–26		.008		.008			.008	None, mottled	Brown
6–18–22		.008			.008	.008		Bluish green	Brown
6–18–26		.008			.008		.008	Mottled, no crystals	Bright dark green
6–22–26		.008				.008	.008	Mottled, no crystals	Green
10–14–18			.008	.008	.008			Pale green	Pink
10–14–22			.008	.008		.008		Pale green	Pink to gray
10–14–26			.008	.008			.008	Few green crystals	Bright brown
10–18–22			.008		.008	.008		Light blue	Pink
10–18–26			.008		.008		.008	Mossy green or brown	Shiny brown

Table (*Continued*)

Blends	Molecular equivalents of color added					Moderate color concentrations	
	CuO	UO$_3$	NiO	FeO	Cr$_2$O$_3$	Crystal	Background
10–22–26	.008			.008	.008	Few, brown	Brown
14–18–22		.008	.008	.008		Pale green	Yellow
14–18–26		.008	.008		.008	No crystals	Shiny green
14–22–26		.008		.008	.008	Mottled, green	Shiny green
18–22–26			.008	.008	.008	None	Brown

Using members 4, 8, 12, 16, 20, 24 and 28, two- and three-member combinations constituting a series of strong color concentrations were blended as follows:

Blend	Molecular equivalents of color added							Strong color concentrations	
	CoO	MnO	CuO	UO$_3$	NiO	FeO	Cr$_2$O$_3$	Crystal	Background
4–8	0.05	0.05						Dark blue	Dark brown
4–12	.05		0.05					Dark blue	Dark brown
4–16	.05			0.05				Very dark blue	Light brown
4–20	.05				0.05			Dark blue	Greenish brown
4–24	.05					0.05		Dark blue	Dark brown
4–28	.05						0.05	Dark green	Brown under-fired
8–12		.05	.05					Normal green	Dark brown taupe
8–16		.05		.05				Fawn	Brown
8–20		.05			.05			Few gray-blue crystals	Dark mottled buff or tan
8–24		.05				.05		Dark fawn or new brown	Brown
8–28		.05					.05	None	Shiny brown
12–16			.05	.05				Dark green	Dark brown taupe
12–20			.05		.05			Mossy gray	Goldstone
12–24			.05			.05		Dark green	Mossy brown
12–28			.05				.05	None	Shiny brown
16–20				.05	.05			Pea green	Green
16–24				.05		.05		Yellow or cream	Brown
16–28				.05			.05	None	Shiny green
20–24					.05	.05		Few, brown taupe	Goldstone
20–28					.05		.05	Brown	Dark brown
24–28						.05	.05	None	Dark brown

Three Color Blends

Blend	CoO	MnO	CuO	UO$_3$	NiO	FeO	Cr$_2$O$_3$	Strong color concentrations	
								Crystal	Background
4–8–12	0.033	0.033	0.033					Dark blue	Brown to dark brown
4–8–16	.033	.033		.033				Dark blue	Brown
4–8–20	.033	.033			0.033			Dark blue	Brown
4–8–24	.033	.033				.033		Dark blue	Goldstone
4–8–28	.033	.033					0.033	None	Bubbled (underfired)

TABLE (*Continued*)

			THREE COLOR BLENDS					Strong color concentrations	
Blend	CoO	Mno	CuO	UO_3	NiO	FeO	Cr_2O_3	Crystal	Background
4–12–16	.033		.033	.033				Blue	Buff to brown
4–12–20	.033		.033		.033			Blue	Reddish brown
4–12–24	.033		.033			.033		Blue	Dark green
4–12–28	.033		.033				.033	None	Dark green, bubbled
4–16–20	.033			.033	.033			Blue	Gray
4–16–24	.033			.033		.033		Blue	Brown
4–16–28	.033			.033			.033	None	Green (underfired)
4–20–24	.033				.033	.033		Dark blue	Goldstone
4–20–28	.033				.033		.033	None	Bubbles
4–24–28	.033					.033	.033	None	Bubbles
8–12–16		.033	.033	.033				Pale green	Brown or buff
8–12–20		.033	.033		.033			Pale green	Brown or buff
8–12–24		.033	.033			.033		Green	Mottled taupe
8–12–28		.033	.033				.033	None	Bubbles
8–16–20		.033		.033	.033			Green	Brown
8–16–24		.033		.033		.033		Dark green	Brown
8–16–28		.033		.033			.033	None	Shiny brown
8–20–24		.033			.033	.033		Gray-blue	Mottled buff
8–20–28		.033			.033		.033	None	Bubbled green
8–24–28		.033				.033	.033	None	Brown
12–16–20			.033	.033	.033			Dark green	Reddish brown
12–16–24			.033	.033		.033		Green	Brown
12–16–28			.033	.033			.033	None	Brownish green
12–20–24			.033		.033	.033		Blue-gray	Goldstone
12–20–28			.033		.033		.033	None	Green
12–24–28			.033			.033	.033	None	Brownish green
16–20–24				.033	.033	.033		Olive green	Dark green
16–20–28				.033	.033		.033	None	Bubbles
16–24–28				.033		.033	.033	None	Bubbles
20–24–28					.033	.033	.033	None	Bubbles

Inasmuch as these were blended by weight, a small error is introduced due to the different molecular weights of the coloring materials. This

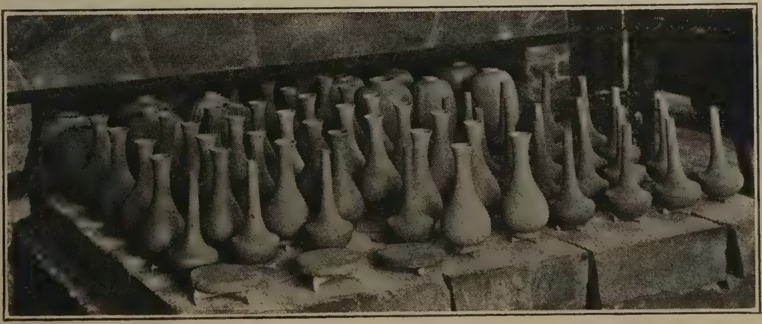

FIG. 2.—Photograph of loaded car entering tunnel kiln.

per cent is not serious, however, except perhaps in the case of uranium and chromium oxides.

Each member of these two- and three-color series might be represented as the members of triaxials. In this case, however, the triaxials consisting, for instance, of end members 2, 6 and 10 would yield for this study only the binary members 2–6, 2–10 and 6–10, and the one ternary member 2–6–10. A more complete study would, of course, cover more members of such triaxials as well as varying the concentration of color in the end members and interblending strong and moderate color combinations. This, however, becomes a matter of mechanical mixing of glazes.

Conclusions

1. The method of introduction of soda should make these glazes more accessible to many desiring to use them, particularly those who do not have suitable equipment for fritting and grinding these frits.

2. A somewhat rapid increase of temperature from about 1000°C up to the maturing temperature of the glaze seems more important for the development of prolific crystallization than slow cooling.

3. The most interesting development of color in crystals is obtained by blending glazes containing less than 0.05 molecular equivalents of coloring oxides.

4. The most interesting textures are found among the mixtures containing a total color concentration of approximately 0.10 molecular equivalents. These textures are particularly interesting on surfaces where the glaze has an opportunity to spread the color segregations along the vertical sides of the piece. Unusual backgrounds are obtained in this manner.

5. The preferential color absorption by the crystals seems to be in the following order:

(*a*) Cobalt is absorbed in large amount and the color of the crystal deepens to almost a blue-black before the glaze is affected. The brown color of the background is intensified with the cobalt additions.

(*b*) Copper is retained by the glaze with no noticeable amount of volatilization. The green color is totally absorbed by the crystal, but pink in fringes around the crystals and in some portions of the background is prominent when copper is used. This darkens to a reddish brown segregation in a green background when the color goes to 0.10 molecular equivalents.

(*c*) Manganese is not absorbed as much as the cobalt and copper oxides and the color of the background darkens with increase of color.

(*d*) Nickel and iron act very much alike as regards their being absorbed by the crystal except that nickel begins to prevent crystallization at about 0.05 molecular equivalents, whereas FeO may be added up to 0.2 molecular equivalents, the background darkening in color faster than the crystals, and crystallization not being affected.

(*e*) Uranium is not absorbed appreciably enough by the crystal to be noticeable. Under reducing conditions, black or bronze colored crystals can be obtained with 0.10 equivalents.

(*f*) Chromium cannot be used as a colorant in this glaze. It prevents crystallization even with only 0.01 equivalents addition.

NOTE: The results obtained by the use of these glazes seem to refute the statement that they are ceramic curiosities and commercial impossibilities.

FLINT FAIENCE TILE COMPANY
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FURTHER DEVELOPMENT OF AN AUTOMATIC KILN STOKER[1]

By John D. Martin

Introduction

Last year I read a paper concerning the development of an automatic kiln stoker, and stated that at that time we had been engaged in this work for a little over two years. Now, after three years we believe we have this problem well in hand.

We have wanted a dependable machine which we could install on a down-draft periodical kiln, which would feed automatically the same amount of cheap coal into each fire box of the kiln. We have wanted to discharge the ash automatically and do away with any serious clinker troubles on the furnace walls or on the grates. We have wanted to provide at the same time ample mechanical circulation through the kiln for watersmoking and provide forced draft to our fuel bed to burn the coal rapidly. And finally, we have wanted to make an outfit of this character pay a large return on the investment because we have not gone into this merely as a scientific experiment to determine if it is possible to fire clayware with automatic stokers—which fact we settled to our satisfaction three years ago, but our idea has been to determine if good automatic kiln stokers are a good investment for ourselves. If such would prove to be the case, they can no doubt be shown to be a good investment for other manufacturers of clay products who like ourselves, have an equipment of down-draft kilns which they are anxious to keep in operation if they can materially decrease their firing costs. (Periodic kilns have certain advantages from an operative standpoint too well known to all of us to require any explanation here.)

At the time we determined to try a stoker, there was no stoker being manufactured for this purpose, and as far as we could determine there were no industrial stokers being made for any purpose having the small capacity required, which is about 150 lbs. of coal per hour as a maximum. Kiln stoking requires a number of small units operating together and such operation presents the problem of so joining and driving these units that the expansion of the kiln and the stoker setting will not bind or cramp the operation of the individual stokers or their driving mechanism. It is a well-known fact that the average kiln does not stay exactly as it was built; the walls expand and creep outward even in spite of the application of the general run of kiln bands. An important part of the stoker problem is to provide the necessary flexibility of the driving mechanism and the connection of this to the stokers themselves so that any change in the position of the stoker settings is automatically taken care of. In addition to this it is necessary that each stoker should be so connected to the driving mechanism that in case its operation is temporarily interfered with, it can be shut off and the other stokers can continue operation. Rather than attempt to adapt any existing industrial stokers to these conditions, it seemed better to start at the beginning and work out the larger problem thus presented as a whole.

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[1] Presented at the Atlantic City Meeting, Feb., 1923 (Heavy Clay Products Division). Recd. Feb. 27, 1924.

Stoker vs. Coal Feeding Device

Our first stokers were merely a coal feeding device which required the fires to be cleaned by hand at about six-hour intervals. We employed a horizontal pipe which fed fine coal through it by means of an auger to a point underneath the center of a round flat grate from where the coal was fed upward through a vertical pipe by another auger through a hole in the center of the grate. The coal naturally pushed itself outward toward the edges of the grate as the feed continued. The bag wall was set around the edge of the grate about six inches away from it. About half the grate was set in the kiln wall. Coal was fed into the horizontal pipe by gravity from a hopper placed over its outer end. We used a wind box underneath the grate into which the forced draft was supplied and this had to be cleaned out at intervals of siftings which fell through the grate. With this arrangement we were able to secure a very considerable fuel economy when firing face brick, and to cut the time of firing from eight and nine days to about five days.

This arrangement taught us the real difference between an automatic stoker and merely a coal feeding device. We saw that we had accomplished the latter only which took entirely too much labor to operate and that between cleaning periods of a reasonable length, our fires were too dirty to be burning efficiently.

A real automatic stoker is not only a coal feeding device, but it will keep the fuel bed in a uniform condition because it keeps it moving uniformly from the time it enters the furnace as coal, until it is discharged as ash. To keep the fuel bed in this condition is well worth while because the problem is not merely to burn coal in the furnace, but to get the heat from this burning coal circulated through the ware from the top to the bottom of the kiln. A coal feeding device which has first a comparatively thin fire on the grate which thickens and becomes dirty as more and more fuel is fed in, is gradually choking off the circulation through the fuel bed and the kiln. With such a varying condition of the fuel bed, the rate at which it will burn the fuel is constantly changing, as a clean thin fuel bed will burn coal faster and liberate more heat. We were confronted also with the usual objectionable loss of heat experienced when cleaning kiln fires by hand.

Development of the Stoker

After firing a number of kilns of face brick in 1921 with these coal feeders, we determined to change them to real stokers, and our first effort in this direction was to change the shape of the grate from round to rectangular, and to lengthen out the horizontal stoker pipe so that the vertical pipe would discharge up through the inner end of the rectangle, that is, that side of it which was nearest the center of the kiln. The bag wall was built in rectangular shape around the edge of this grate, part of the grate being in the kiln wall as before. Our idea was that the fuel bed would thus be constantly working its way over the grate from the rear toward the furnace door and the ashes would accumulate right inside this door from where they could easily be removed simply by opening the door and taking them out with a shovel. We tried this grate level and also on a slope from the rear toward the furnace door and found that the fuel bed did not move uniformly toward the door in either case. The unburned coal did, but the ashes underneath did not, and this resulted in an accumulation of ashes immediately on top of the grate with a layer of unburned coal over it. These ashes could not be removed without taking out at the same time a considerable amount of unburned coke. We also had a bad accumulation of clinker on the furnace walls.

The reason this idea was not practical is because of the behavior of fine coal during the burning process. When first introduced into a furnace, it will flow readily until the coking process is well on its way, when it will commence to form rather large masses of coke which will not flow so easily. When it has become ash, slightly fused and somewhat cooled, it will flow less readily than either the green coal or the coke, this being especially true if the ash is in contact with the grate. This explains why our fuel bed refused to move uniformly toward the furnace door. Although our grate was very much smaller, our problem was apparently the same as encountered in the design of the largest boiler stokers which have a grate area twenty-five feet square carrying as much as twenty-five tons of coal when in operation.

We therefore designed a rectangular shaped grate with moving members to carry the whole fuel bed toward the furnace door as we did not want to resort to any kind of dumping grate which would fill our wind box with ashes or siftings. After we had all the parts ready to assemble, we discarded this outfit without even trying it out because we decided to go back to the round grate idea as a better means to prevent the formation of clinker on the furnace wall. If we could keep the fuel bed from touching this wall, or at least have it very thin there, we were sure we would have no clinker formation.

We believed we could accomplish this by means of a rotating round grate having the fuel fed to it from the center from below as in our original layout. In place of a flat grate we have raised it in the center so that it is approximately the shape of a cone. When the kiln is on high fire, the grate is rotated once in about thirty minutes and the ashes are taken off its outer edge continually by a scraper. They fall into the ash pit outside the wind box where they can be reached easily by the fireman with his shovel.

At this time last year we had developed the best means of rotating this grate; we had to discard shafting and gears on account of the warpage of the parts. We had settled on the construction of the grate itself with a rather novel design to give us a large percentage of free opening through it for the passage of the draft and at the same time restrict greatly the falling of siftings through it. We had also found a method of automatically removing such siftings as actually fell into the wind box, and we were fairly successful in preventing clinker formation on the furnace wall without having to resort to special wall construction employed in larger stoker layouts to overcome this trouble.

Refractory Kiln Equipped

We equipped a twenty-eight foot round down-draft kiln with eight of these stokers at a plant making refractories. We have fired this kiln several times with a coal which is of a very different character than the coal used when developing the stoker at New Straitsville. This coal has shown a much greater tendency to form large chunks of coke on the grate and hard clinker on the furnace wall. We have found a means of preventing this coke formation which keeps the fuel bed open to the draft and we are working on the clinker problem with what we believe is a very good chance of success. We found it necessary to remove the clinker once only from about half the furnaces during the five and one-half days of the burn, and while there was some clinker on the walls of the other furnaces, it caused no trouble of any kind and was allowed to remain. The difficulty is no greater in removing these clinkers than is encountered in taking them off the walls of a hand-fired furnace but we wish to avoid any such work of this character about the kiln as our aim is to have the firing labor consist only of shoveling coal into the hoppers and ashes from the ash pit.

We have hand-fired kilns of the same type at this plant on which we have as many as twelve furnaces having a total grate area of about seventy-two square feet. Each stoker has seven square feet of grate area so that the eight stokers on this kiln have but 56 square feet. Yet with this reduced number of furnaces and grate area we have shortened the time of firing from an average of $7^1/_2$ days for the hand-fired kilns to $5^1/_2$ days. In each case a cone 5 was put down located 9 inches above the floor. In firing a kiln set with the same tonnage of standard fire brick shapes I believe we could reduce this time to less than five days because we could watersmoke these quicker than the ware we have been firing which has consisted largely of locomotive firebox arch shapes some of which weigh considerably over one hundred pounds.

In firing with natural draft hand-fired kilns it is generally the practice to attempt sometime during the burn before the finishing temperature is reached, to stop raising the temperature in the top and soak the heat to the bottom, after which the heat is again raised in the top to the finishing temperature and held until the bottom is finished. To push the top as rapidly as possible to a finishing temperature and pay no attention to the bottom in the meantime, generally results in trouble. Yet this is exactly how we fire this kiln because with a thin hot fire we get a very rapid circulation through the fuel bed and the ware which raises the heat in the bottom very quickly. At the finish of our last firing, which required $5^1/_2$ days, we had a cone 6 down $5^1/_2$ feet above the floor level of the kiln and a cone 5 down 9 inches above the floor.

At no time during the last 18 hours of the firing was the difference in temperature between the top and bottom cone greater than 50°, and some of our readings showed a difference of only 25°. The temperature of the upper cone brick was raised from 1550° to 2150°, its finishing temperature, a difference of 600° in 36 hours, this being at the rate of 400° in 24 hours. You will note that this was not a pyrometer reading taken through the crown of the kiln, but was the actual temperature of the cone brick itself obtained by means of an optical pyrometer. During this time we had high temperatures in the furnaces around 2500°, the highest noted having been 2675°, and it is worthy of note that these were secured with a draft pressure just before entering the windbox as low as .2 of an inch.

Poor Grade of Coal Handled by Stoker

We are burning a grade of coal with these stokers which usually sells for very much less than run-of-mine or lump and which is known in our district as fine coal and is sometimes called slack. In the last few months we have paid as low as eighty-five cents per ton for this coal although recently the price has been advancing. On the other hand we have been paying three dollars per ton for lump coal of a suitable quality for our hand-fired kilns. These prices are f. o. b. the mine. There is very little use for this fine coal except to burn it with automatic stokers, yet the mines have to produce it when loading lump coal and at times it becomes a drug on the market. It is becoming more and more the practice of enterprising buyers to store large quantities of it at such times. Although it contains a considerable amount of dirt our stokers burn it readily. While the augers will not feed through pieces too large to go through an inch ring, they will crush such chunks down to size first and then feed them and I have seen pieces as large as a man's fist disposed of in this way. However, too many pieces of this size would interfere with the capacity of a stoker as it is primarily a feeding device at the hopper and not a crusher.

Savings Effected

Coal.—The stokers will effect a saving in the cost of firing not only in the amount of fuel required but in its price. The saving in the amount of fuel will depend on whether the previous hand-firing practice has been good, bad or indifferent, and whether mechanical draft has been used or not. The saving in the price of the fuel will of course depend on the coal market, and the maximum amount here will be obvious when it is understood that mine run or lump coal frequently costs two or three times as much as fine coal at the mines. Having recently had the advantage of such a favorable coal market, the saving made on our last burn per thousand brick basis was over $2.00.

Upkeep.—The upkeep of these stokers should be very low as they are a slow motion machine, and there can be a very considerable warpage of the parts carrying the fuel bed before the mechanical action of the stoker would be interfered with. The drive shafting running to each of the stokers turns over at only five or six revolutions per minute when the kiln is in high fire. At the same time the augers are turning at about three revolutions per minute and the grate itself revolves only twice an hour. The grates consist of five separate castings of a very simple construction and they could be very easily and quickly renewed if necessary without the use of any tools—not even a wrench would be required.

Each stoker will require about $^1/_{10}$ h. p. to operate it. The low-draft pressure used means a minimum of power for such service. For the average round kiln I would say that less than 2 k. w. per hour would be ample.

Summary

We can sum up the reasons for expecting economy from our stoker installation as follows:

1. On account of its ability to burn cheap coal.
2. Because of the saving in fuel tonnage due to the burning of the coal under more efficient conditions.
3. Owing to the high furnace temperatures which allow the kiln to be fired off in a shorter time. This means a smaller proportional loss of heat from the stacks and by radiation from the kiln crown and walls.
4. There is no loss of heat such as is usually experienced when fires have to be cleaned.
5. The furnace arches and walls are not subjected to the varying temperatures experienced with hand firing.

6. Owing to the forced draft we are independent of atmospheric conditions and can fire closer to schedule time.

7. We can shorten the turnover of the kilns and get more ware through them.

8. We believe we will decrease the labor cost of firing. Firing with these stokers should not be the hot job which requires the firemen of hand-fired kilns to have so much "time out" which now generally amounts to about thirty minutes out of every hour.

9. Where any flashing of the ware is objectionable, this can be entirely avoided. After the sulphur smoke ceases, there is not even a thin haze of smoke comes from the stack.

10. Circulation through the kiln is so rapid during the watersmoking period, that the danger of the ware in the bottom soaking up moisture, getting soft and kiln marking is reduced to a minimum.

In conclusion I would say that the larger part of our time since we took up this work has been spent in development and not in actually firing ware, but that the good features of stoker firing have nevertheless been so persistent and so marked in the runs we have made, as to be unmistakable in their meaning.

STRAITSVILLE IMPERVIOUS BRICK CO.
NEW STRAITSVILLE, OHIO

Discussion

PROF. WORCESTER: Mr. Martin, have you had any difficulties in holding the top of the kiln from overheating by the steady fire that would be obtained from the stoker, that is, a continuous feed in the stoker? Ordinarily we think that we must have an interval between fires to let a certain amount of air pass through our kiln to drive the excess heat from the top down, but (1) is there any difficulty with the mechanical stoker? (2) Are you able to flash with it?

MR. MARTIN: In answer to your first question, you state that it is generally considered good practice to allow an amount of air to enter the kiln over the fires between firing periods in order to carry the heat away from possibly overheated heads to the bottom of the kiln. We do that because we do not have a steady application of heat at a uniform temperature. Just before the firing period the temperature is low. The kiln is fired and a few minutes afterward the temperature rises to a comparatively high point and it is because the curve is going up that you have to go down. If we have a means of providing a steady application of heat we do not have to go so high with the temperature during the application of heat. Consequently we do not have to go below the average at any time. It is possible to use a temperature from the fire boxes that is much higher than the finishing temperature until the time we are going to do the finishing. That is, we can subject the ware to a higher temperature as long as it has not reached the maturing temperature, but when the ware commences to reach this temperature naturally we have to cut down the temperature of the gases to about what would be the finishing temperature, so that the ware is not overfired. The fuel bed on the grate of the stoker is very light, and as forced draft is used, we get an unusually rapid circulation through the kiln from top to bottom which heats the ware in the bottom of the kiln very rapidly. It is only after the finishing temperature is reached in the top that we have to stop and wait for the bottom to heat up.

So far as flashing is concerned, we have not tried to do any flashing with the stokers, because they were developed at our face brick plant where we undertook to prevent flashing. That was one of the things we were trying to avoid and why we chose the underfeed type of stoker. This stoker will make a minimum amount of smoke. Whether it is going to be possible to flash ware with this stoker installation or not I am frank to say I do not know.

Mr. Stevens: How much power did it take?

Mr. Martin: One-tenth of a horse power required for each stoker.

Mr. Thropp: How did you take care of the clinker?

Mr. Martin: In designing the stoker the idea was to take care of the clinker by preventing its formation. We have clinker in two different places, on grates and on furnace walls. With very thin fire and the stoker operated properly the fire will tail so none of the fuel bed will get in contact with the furnace wall. If we have no slag in contact with the furnace, naturally we are going to get no clinker on it. The ashes being taken off from the edge of the grate, the grate will rotate and before it gets around again to the place where we take the ashes off, there will not be enough fuel bed thickness built up against the furnace wall to have any clinker trouble.

As far as the clinker trouble on the grate itself is concerned, that depends pretty largely on the character of the coal you are using. There are some coals that will not clinker badly on the grate. There are some coals that run down on the grate, forming big slabs which shut the air off. There are places where they use oyster shells and limestone mixed in with the fuel in order to prevent that sort of trouble. It does well for a while but it is a difficult matter to contend with.

Mr. Thropp: How about the combustion arch that takes care of the gases?

Mr. Martin: You are acquainted with the ordinary kiln furnace construction. In our case we have a very small furnace. This bag wall gets very warm and aids ignition. The stoker has its grate center under the inside edge of the kiln wall. In the ordinary hand-fired kiln after the ware reaches the ignition temperature of the gases we have the very best condition possible for good combustion and complete combustion, and under such favorable conditions we can get an impressive idea of one of the failings of hand-firing methods by watching the smoke pour from the stacks after they are fired. When our stoker kiln is on high fire, we do not get even a thin haze of smoke from the stack—it is absolutely smokeless.

MR. HARROP: Mr. Martin, do you use any water or steam to prevent clinker formation?

MR. MARTIN: That is a well-known means to soften up clinkers so they can be easily removed. It does not actually prevent them although it may have some tendency toward that. I do not think I would want to resort to that because there is a certain part of the mechanism below the grate which would rust under the action of steam. While they are cast iron and would not show bad effects from the rust quickly, it is rather doubtful whether that would be good mechanical practice. There is no iron work of any kind above the fuel bed. It would be suicidal to attempt anything of that kind because we would burn it out. We have to keep all the mechanism below the fuel bed and steam and moisture would interfere to some extent, although it might be well to adopt that means if we could get rid of the clinker trouble with it.

MR. BROOKS: Have you considered the possibility of an inexpensive clinker grinder? In the use of underfeed stokers in power plant work one of the principal difficulties has been the problem of removal and ejection of clinker. In selection of stokers very frequently the answer to the question of clinker elimination decides whether an underfeed or chain grate stoker should be installed. Have you considered individual motor drive for each of the various stokers on each of the bags? It would also be interesting to know what percentage of combustible you find comes through the grates with the ash and refuse.

MR. MARTIN: On all the modern later developments of automatic stokers used in boiler practice, they are resorting to clinker grinders but I do not think we are having trouble that would be avoided by the use of the clinker grinder. That is a way of getting rid of the clinker after it is formed. What we are trying to do is to prevent the formation of the clinker in the first place. If I should get the clinker to a place where I would have a clinker grinder, I would find a means of ejecting that clinker without having to resort to a grinder. We have not had any big clinkers formed in the fuel bed. In fact, with a fine coal we generally find a large percentage of dirt that sometimes helps to keep the clinker from forming.

The next point that was brought up was about individual drives. That would be more expensive than the scheme we are using to drive the stoker with shafting. The total power requirement for a kiln as far as the stokers themselves are concerned is one-tenth of a horse power for each stoker. If we have ten stokers on the kiln, we have only one horse power required. A one and one-half horse power motor would supply that.

Mr. Brooks: Individual motors driving each individual stoker in each bag was what I had in mind.

Mr. Martin: With the individual motor you would have to have ten small units and they would cost more than the one unit of one and one-half horse power. In other words, you could not buy ten one-tenth horse power motors for what you could buy one one-horse power motor.

Mr. Brooks: The saving would be on operating cost, elimination of line shafting bearings, line shaft friction, and line shaft maintenance. You mentioned having used wooden shearing pins to relieve the strain in case the feeder mechanism became clogged. These wooden shearing pins have been used for many years in boiler plant practice and have given considerable trouble. Very frequently workmen in replacing a pin do not take the time and trouble of going to the storeroom to get a standard shear pin as supplied by the manufacturer but stick a nail in instead. Motor drive, however, lends itself better to emergency control than engine drive as one can use a circuit breaker with an alarm attachment which immediately indicates to the superintendent when the stoker ceases functioning.

Mr. Martin: You will always have that sort of thing to contend with. We have it in our plant. For instance, we have a spiral feed under a bin that gets clogged sometimes and we have to have a break arrangement there. A bolt runs through. I go in once in a while and find there are two bolts in there. Some time it is going to break something that is of vastly more importance than a bolt. We have also another feature of the same character in the mechanism that revolves the grate. There is a possible chance some time that clinkers will cause stoppage and so we employ a little link that we saw off the end of an inch and one-half pipe It is about one-sixteenth of an inch thick. It drops down over two pins and in case we have stoppage of the grate for any cause or other that link breaks first and saves breakage of any more important parts. It is a simple matter to find out what the trouble is and drop in another link on there.

Mr. Jackson: As I understand it, it rotates on a vertical axis once in every thirty minutes and the ashes are all scraped off by a scraper only at the front, except what happens to fall down at the back.

Mr. Martin: There can be nothing fall down at the back. It is all closed except at the front. There is a sixteen-inch slot four inches high above the edge of the grate in front. That is the only place where the ashes can be thrown out except through the door in case of an emergency.

Mr. Jackson: You described a little worm shaft underneath the grate for taking the ashes off.

Mr. Martin: That is for siftings. As a matter of fact much stuff cannot fall through the grate.

Mr. Rice: Have you had an analysis of the ash siftings and do you know what percentage of combustible matter is getting through?

Mr. Martin: I have not undertaken to convey the impression that this is a finished machine and I have nothing I want to conceal about it. We are getting entirely too much combustible in the ashes and we are taking steps to control that. I have not had an analysis yet but it is entirely too high, and yet even with that condition we are showing a saving of from 20 to 30% in the amount of tonnage required to fire the kiln over hand-firing methods.

Mr. Rice: Do you reburn the siftings?

Mr. Martin: We do not get from one burn from one of these kilns more than two bushel basketfuls of siftings. It would be a very simple matter to do that but here is something that I am going to attempt to do. If I cannot prevent too much combustible in the ashes I am just going to go the other way and force the stoker to throw out a great deal of combustible. It will have the gas practically all worked out of it. I am going to use that stuff again to watersmoke the next kiln. It will be sootless and will make no smoke.

Mr. Bole: How thick does it build up?

Mr. Martin: The fuel bed should taper off to nothing at the edge of the grate. It would not be over four or five inches at the top. That is a very thin fuel bed and we keep it open on a couple of stokers that we are trying out this way by raising the last two rings at intervals with a very simple mechanism, raising them about an inch and letting them drop. That prevents the formation of coke in masses in the top, breaks open the fuel bed and allows the draft to pass through very easily. We use forced draft pressure just before it enters the wind box of about three-fourths of an inch.

If we use more draft than this on this particular kiln we blow the burning gases out around the edges of the furnace door which we do not consider good practice. We use just enough draft to prevent any suction of air into the furnace around the furnace doors or through the ash outlet, such air as is generally called secondary air which we find we do not need to secure complete combustion.

The forced draft relieves the stack of the frictional load of pulling the combustion air through the fuel bed which will result in a more rapid circulation through the kiln and the stack itself so that the stack will appear to be drawing more freely. While we have not actually increased the pull of the stack, we do increase the circulation through it by having relieved it of part of its load.

FIRING REFRACTORY BRICK IN A ROUND DOWN-DRAFT KILN WITH A MECHANICAL STOKER[1]

By E. E. Ayars

ABSTRACT

An outline of firing tests conducted on round down-draft kilns to develop a mechanical stoker for use in firing fire brick and other refractories. Stoker used has been applied to terra cotta kilns with considerable success but it appears that the larger sizes of kilns are not easily handled with this type of stoker. Further tests may develop something in the way of technique which will show a reduction in firing time. Fuel consumption has already been reduced and uniformly fired ware secured. The time element is of great importance in plant capacity.

Introduction

Mechanical kiln firing methods have been frequently discussed by plant operators, and their adoption when perfected will reduce firing to something like an exact science. In an attempt to secure flexible operation and maximum fuel economy many new types of kilns and special devices have been brought forward from time to time. For certain classes of ware the continuous chamber kiln fired by producer gas or natural gas has proved successful. Oil firing has been adapted to round down-draft and rectangular kilns firing a variety of products. The car-tunnel kiln has been applied to many products and the fuels used include natural gas, producer gas, oil and coal.

New methods are difficult to introduce and often entail great expense. The majority of manufacturers of ceramic products have moved with such caution that comparatively few plants are burning oil or gas, although both of these fuels have their advantages and special fields.

It should be noted that a small percentage of all refractory materials produced are being fired by oil or gas and a still smaller percentage being fired in car-tunnel kilns. Enormous tonnages of fire brick are now fired in both round and rectangular kilns, coal being used for fuel. Irregularities in operation are costing the fire brick maker large amounts of money each year and the results obtained and fuel consumed on some plants would almost cause a graven image to weep. Many fire brick plants in this country are overfiring portions of their kilns and underfiring other portions. The cause of these results is not all in the firing method. Most of it lies in poor kiln construction or design and poor repair while a certain portion is chargeable to indifferent setting.

The special refractory materials such as magnesite, chrome and silica brick are generally fired with more care. This is possibly accounted for by the fact that more attention must be paid to kiln equipment, setting

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[1] Presented at the Atlantic City Meeting, Feb., 1923 (Refractories Division). Recd. May 2, 1924.

and firing methods in order to reach the high firing temperatures employed. It is certain that the indifferent treatment afforded refractories fired from cones 4 to 10 would never produce results in firing kilns from cone 16 to 20.

There will continue to be used large numbers of fire brick kilns consuming coal for fuel, but this fuel must be used more economically. It appears that any suitable mechanical method which would permit a closer regulation of fire box conditions would be a paying proposition, and there is a big field for the kiln stoker.

The stokers applied to boiler operation are of several types and generally speaking much too complicated in construction for average brick kiln use. One company has spent considerable money devising a suitable underfeed stoker of the lateral retort type and in a recent article by the designer reports a reasonable success with it. However, it appears that the use of any complicated stoker grate would increase the cost of the equipment unduly and commit the user to large recurrent bills for repairs and parts replacement. A plant operator is loath to adopt any piece of equipment which may give trouble in operation or which may require frequent repairs. The simpler the grate and the operating mechanism the less trouble will be experienced in service and the fewer repairs will be necessary.

The Gates Stoker

The Gates kiln stoker is the result of the development of a mechanical stoking idea. The grates first employed were common flat bars and forced draft was applied. After several unsuccessful attempts to use forced draft, the stoker was tried with natural draft with more encouraging results. Gradually the present grate, consisting of a cast iron plate provided with numerous holes for the admission of air through the fire bed, was developed.

This grate is fixed in an inclined position to facilitate the forward movement of the fuel bed. A slightly smaller flat grate of similar construction is placed between the back wall of the furnace and the end of the inclined grate. Provision is made for withdrawing the flat grate while cleaning fires and the ash and clinker drops through the opening thus effected into the ash pit.

The fuel is held in a small hopper mounted on the stoker frame directly over the feed slide. Power is supplied by a one-quarter horse power motor which drives, through a combination of gears and friction ratchet, the operating device. All feed slides are linked to the driving mechanism by a $^3/_4$-inch pipe circling the kiln. The stoking motion of the slide is slowly accomplished by the action of a cam against a vertical arm to which the circling pipe is attached. At the conclusion of the charging stroke a coil spring pulls the vertical arm back into a notch in the cam thus effecting the back stroke of the feed slide.

The whole mechanism is simple, easily adjusted for different speeds and has a minimum number of wearing parts.

This stoker was developed on terra cotta kilns and up to the present time has shown steady improvement in results. Recently several of the leading terra cotta producers have installed this equipment and are enjoying a considerable saving in attendance, fuel and firing time, at the same time obtaining a high percentage of first class ware.

A Plant Test

The adoption of the fire-box stoker by manufacturers of other products only awaits the satisfactory demonstration of its adaptability to their problem. The designer chose the fire brick industry as the first field for test and made arrangements with the Laclede-Christy Clay Products Company, of St. Louis, to conduct a test at their Laclede plant. This test was observed by representatives of *Brick and Clay Record* who were pledged to publish an unbiased opinion of the results obtained. The report has already appeared but in its present form is hardly available for publication in the *Journal* of this SOCIETY.

In order to obtain data which would permit comparison of common practice and stoker firing a thirty-two foot round down-draft kiln was selected and fired off by the hand method. The kiln was in good physical condition and the setting consisted of sleeves, runners and nine-inch brick. The kiln, of the open bottom type with a continuous bag wall, was equipped with ten fire boxes, each having a grate area of 1,005 square inches. Flat grates were used. The amount of ware set was 164 tons. The average practice of the plant shows a fuel consumption of forty-four tons and a firing time of 132 hours for such a setting. Although the stage had not been set for any records there was a spirit of competition in the air and as might have been expected a record for fuel consumption and firing time was made. The ware was of the usual high quality.

The fuel consumption was 39.34 tons and the firing time 120 hours which shows an all-round efficiency of 111% based on common plant practice. The fuel used was Franklin County, Illinois, run of mine.

It should be noted in passing that the Laclede-Christy Clay Products Company have expended a great deal of effort on their firing practice and have developed their methods to such an extent that they are getting unusually good results in firing time, fuel consumption and quality of ware. The designer of the fire box stoker was fortunate in being able to make his tests on a plant where the standard practice is of such a high order. The head fireman, a man of several years' experience, gave excellent coöperation, and the suspicion with which many new devices are received on a plant was notably absent from the minds of the plant executive force.

As soon as the hand-fired test kiln was drawn the stokers were installed and the kiln reset with similar ware for the stoker trial.

The stoker used was of identical size with that installed on terra cotta kilns, which are usually much smaller and of the muffle type. The grate area of each fire box was 603 square inches or $^6/_{10}$ of the original fire-box area. The reduction in area was caused by cutting the width of the grate to eighteen inches. The length remained the same as formerly.

Inasmuch as the stoker operators were not familiar with the open fire kiln it was suggested that a trial firing be run off before the formal test was undertaken. This gave opportunity to study the firing conditions and while the results were not very good with respect to fuel consumption and firing time, the ware drawn from the kiln was first class. The amount of ware set was 201.7 tons. The firing time was twenty hours longer than the accepted standard practice. Fuel consumed was 48.5 tons.

The fuel used was Franklin County, Illinois, screenings which had been in storage on the plant for some months. It was so dirty and low in heat units that its handling presented quite a problem. At the end of the firing it was necessary to break up the lumps in some mine run coal and feed it to boost the heat and flash the brick.

The stoker is used very successfully with screenings from other coal fields but the slaked screenings available for this firing did not measure up to the occasion. The dirt proved a source of trouble and the coking tendencies of the coal caused it to cake on the grates after the first sixty hours. A large proportion of the fuel was thus pushed through the stoker without firing and its heating value lost to the kiln. However, considering the fact of heavy tonnage and tight setting the fuel consumption was not unduly high. The extra time consumed in firing was to be expected in view of the radical change in method and the poor fuel available.

The Second Stoker Trial

The second stoker trial which was observed as a test firing by representatives of *Brick and Clay Record* was of considerable interest. In view of the difficulties in using the dirty screenings on hand a fresh supply of washed screenings was secured from the same coal field. This coal is termed No. 3 and No. 4 nut by the trade and is somewhat cheaper than run-of-mine, but a little more expensive than straight 2-inch screenings. The fuel burned very freely and gave no trouble with coking on the grate. From the writer's experience the coal appeared to burn too freely as it made a flashy fire and the fire box did not seem hot enough to insure the best results at all times. Clinker formed high up on the back wall of the fire box during the later stages of the firing, and while it was somewhat difficult to reach in, cleaning did not affect the fuel bed as clinker formed on the grate would have done. Good combustion obtained at all times during the firing and the amount of combustible left in the ash was much less than with hand-firing methods. 5.95 tons of ash was left from the hand-fired test and 29.24 tons of coal consumed. 2.5 tons of ash was noted on the stoker-fired test, with 41.53 tons of coal consumed.

The amount of ware set was 165 tons. The coal consumption figured .25 ton per ton of ware while with the hand-fired test the fuel consumption was .24 ton per ton of ware. In this connection it should be noted that the cost of the fuel used on the stoker was $0.95 per ton less than that of the hand-fired burn and shows a distinct saving although the consumption per ton of ware is about equal. The ware drawn from the stoker-fired kiln was equal in every respect to that of the hand-fired test.

In the matter of firing time only does the stoker appear to be at a disadvantage. This is a very important item as it regulates plant capacity and if it were found impossible to reduce the firing time the other possible advantages would not warrant adoption of the stoker. However, let us consider the question of firing time in the light of all the circumstances attending the run, and determine what it promises in the way of future development.

A Discussion of Results

It was apparent at the outset of the firing that the grate area was too small for this type and size of kiln. This had been demonstrated in the first trial firing. The effect of low grate capacity is conceded to be a lengthening of the firing time. Often lack of grate surface may prevent reaching the proper finishing temperature, even though the firing may be continued indefinitely. An increase in grate area was indicated as necessary before further tests were made.

Draft has a decided effect on firing time. The draft available in the hand-fired burn was at all times adequate and, on account of a hot tunnel and stack, abnormally good during the early stages of the firing. In the case of the stoker firing the tunnel was not hot to start with and the draft continued subnormal almost to the end of the firing. It was particularly sluggish up to the 100th hour of the firing when some leaking stack dampers were plastered up and the draft improved at once.

Lack of draft lengthened the watersmoking period materially, requiring sixty-four hours to complete as against forty-six hours for the hand-fired burn. A temperature of 920°F, as recorded by the pyrometer, had been reached in the top of the kiln before the moisture cleared from the bottom. This condition affected the subsequent heat distribution and was largely responsible for the increased length of firing time. Closer study of the causes of sluggish draft early in the firing would have resulted in the same remedial steps being taken and less delay in the completion of watersmoking would have been experienced.

On account of the experimental nature of the test the problem was to determine what method of firing with the stoker would give the results required. At the same time a creditable showing on the quality of ware produced, together with a saving in firing time, fuel consumption and labor was expected. Poor draft and low grate capacity provided a physical handicap, while an unfamiliarity with the firing requirements of the ware contributed almost as much to the lengthening of the burn.

The stoker operators being unfamiliar with the open fire kiln found it necessary to depend absolutely on the head fireman for guidance. He, in turn, being inexperienced with the stoker fire exercised a justifiable restraint over the heat raising speed. The fact that very little air entered over the fire with the stoker, while a considerable excess enters with hand firing, left him sometimes at a loss to know just how to proceed to get a desired result. It is easily seen that with stoker firing the same conditions can be maintained over an indefinite period, while with hand firing there is a recurrent cycle ranging from a very smoky condition when the fire is stoked to a clear bright flame just before the next fire is put on. Just what kind of fire to maintain at different stages of the firing was the real problem.

Considerable time was lost at the finish of the firing on account of a misunderstanding by the stoker operators of what was required. The head fireman was satisfied that the top of the kiln was hot enough and to work the heat to the bottom of the kiln requested a long smoky flame. No further attempt was to be made to raise the heat. This order was placed at 124 hours and it was thought probable that the kiln would come off at 136 hours. However, the flame desired was not carried because of the failure of the operator to understand what was required, and at 136 hours the kiln had not moved. When the head fireman realized how little had been accomplished during the night he explained the requirements further and his wishes were followed closely throughout the rest of the day. The kiln came off fire late that night, fifteen hours after it should have finished according to the calculation of the head fireman. As a result the coal consumption was raised a probable seven or eight tons.

In the light of the foregoing argument it appears that the firing time of the test kiln may be very much improved upon. It should be remembered that hand-firing methods have been in use for many decades and in this particular plant have been brought to a high degree of efficiency. Equal results cannot be expected from the stoker in one or two campaigns. However, taking all the circumstances into consideration the results are remarkable and give much promise for future developments.

CLEVELAND, OHIO

FACTORS AFFECTING THE RESISTANCE OF SILICA REFRACTORIES TO ABRASION[1]

By Fred A. Harvey[2] and Earle N. McGee[3]

ABSTRACT

The resistance to abrasion is tested by grinding a groove in the surface of the refractory by means of a carborundum wheel with suitable mounting. Other methods used in the tests are discussed. Factors affecting resistance of silica brick to abrasion are porosity and degree of burn. Porosity is affected by grind, quality of ganister, per cent lime and workmanship. Data are given showing a rough relation between length of groove, porosity and burn.

Introduction

The abrasion of refractories during service has been receiving more and more attention during the last few years. In this respect it merely follows nearly all the other properties of refractories. The consumer is calling for higher fusion point, greater resistance to spalling, greater resistance to slag action and less shrinkage under load. Many companies are specifying these qualities, using either the methods of the A. S. T. M. or their equivalent. A suitable test for abrasion has been discussed informally in many committee meetings and some preliminary work done toward developing a method. Resistance to abrasion has not been embodied in any specifications with which the writers are familiar except possibly in general terms. It cannot be properly specified until there is some numerical measure of the property. The development of a reliable method will give the manufacturer another control test and aid in the production of a uniformly high grade product. The importance of the subject is evident if we consider a few illustrations, such as the grinding action of the coke on the side walls (see Fig. 4) and floor of a by-product oven during the periodic pushing of the coke and withdrawal of the pusher ram; the abrasion of the walls of a blast furnace and of vertical lime kilns as the charge works its way down; the sand blast action of the gases on hot patches in open hearth furnaces; clinkering of vertical gas retorts and the side walls of stoker fired boiler settings. Many other illustrations could doubtless be added.

M. L. Hartman and J. F. Kobler[4] describe an apparatus for testing resistance to abrasion. Their apparatus consisted essentially of a grinding wheel pressed against the surface to be tested. Speed of rotation, time, and pressure being constant, the amount of material ground away was considered a measure of the resistance to abrasion. The apparatus de-

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[1] Presented at the Atlantic City Meeting, Feb., 1924 (Refractories Division). Recd. Oct. 5, 1924.

[2] United States Refractories Corporation, Mount Union, Pa.

[3] Semet-Solvay Company, Syracuse, N. Y.

[4] Kobler, *Trans. Amer. Electrochem. Soc.*, April 8, 1920.

scribed below is similar in some respects to that used by Hartman, the essential difference being that Hartman holds the test specimen against the grinding wheel by a constant force, resulting in a gradually increasing surface being ground away as the wheel penetrates, while in our apparatus a groove of fixed size is ground in the surface of the specimen and after the first few seconds the grinding wheel is always acting on the same amount of surface. Several experiments indicate that Hartman's method is perfectly capable of determining the difference in resistance to abrasion where this difference is large, as for example between carborundum and clay but that it fails to distinguish between two samples of the same class of refractory, such as two silica tile. The method described below has this advantage, that it gives large numerical differences for various tile of the same class.

A third method for testing resistance to abrasion is being tried at one of the large testing laboratories. In this method a sand blast is directed against the surface under test and the amount of material eroded in a given length of time under standard conditions, is compared with the amount eroded from a refractory arbitrarily chosen as a standard. For certain uses this method seems to simulate closely actual operating conditions. It is entirely possible that for these conditions the sand blast method would give the best guide for the production of the most resistant refractory.

All of the tests described below were made on tile at atmospheric temperatures. The assumption is made that approximately the same ratio would hold for both operating temperatures and atmospheric temperatures. It is recognized that this point needs further test though the evidence so far obtained both from laboratory testing of this (cf. Hartman), and other properties and from operating experience indicates that it is not badly in error. It is, of course, much easier to make the tests on cold tile. We have had under consideration for some time a method for making hot abrasion tests and have developed a method so far on paper only. It is hoped to carry out these experiments at a later date.

Description of Apparatus

The apparatus used in the tests described below will be readily understood by reference to Fig. 1. A five-horse power alternating current motor, speed 1800 r.p.m., has a crystolon grinding wheel, 10″ x 1″, mounted directly on its shaft. The wheel is grain thirty, grade "J." Underneath this wheel there is a carriage which moves on tracks parallel to the face of the wheel. The force necessary to move the carriage is supplied in this case by the crude device shown, which consists merely in a bucket attached to the carriage by a window sash cord passing over a pulley. To put the apparatus in operation the brick or tile to be tested is mounted in the carriage at such a height that the wheel will cut a groove exactly one inch deep.

It is then blocked in and clamped tightly by means of the set screws on the side of the carriage. The tracks are wiped clean and the weight in the bucket adjusted until it is just sufficient to overcome the friction of the carriage. A fifteen-pound weight is then added to the weight in the bucket. It consists in this case of the two pieces of angle iron which show in the cut. The wheel is then started and the tile held just out of contact until the second hand of a watch points to 60, when the carriage is released and the wheel allowed to grind a groove in the brick for exactly two minutes. At the end of the two minute interval the carriage is pushed back away from the wheel and the dimensions of the groove measured.

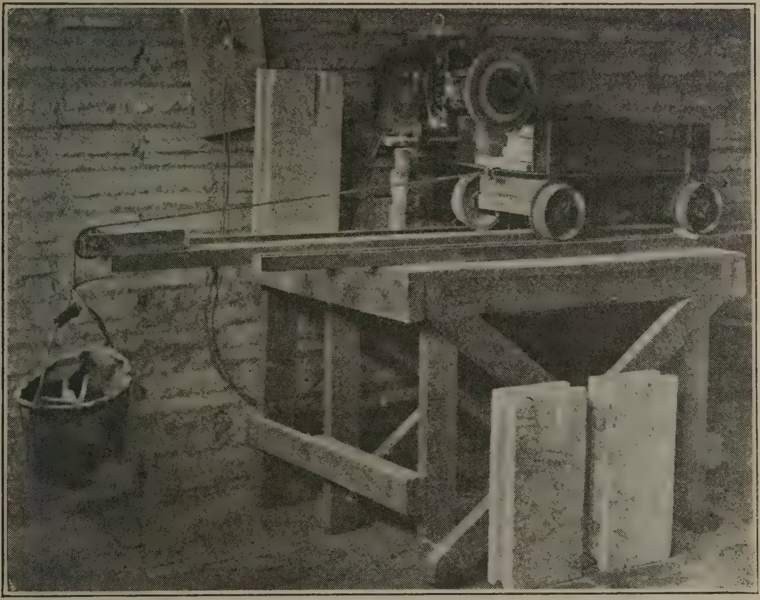

FIG. 1.

The entire credit for this scheme of testing brick for their resistance to abrasion should go to L. D. Huestis of the Portsmouth By-Product Coke Company. Mr. Huestis built the first machine of this type and used it to determine a standard for coke oven shapes.

The apparatus described above has certain defects which can be eliminated by more careful construction. In the first place, the friction is too high. With properly leveled rails and dust proof ball-bearings on the carriage and frequent enough cleaning of rails and carriage, this could be largely eliminated. There is too much side play both in the carriage and the grinding wheel. There is evidence at times that the wheel binds on the side of the groove it is cutting, due to the carriage being out of line, which undoubtedly decreases the length of the cut. On the other hand if the wheel starts jumping the length of cut may be more than doubled. This effect has been eliminated. It was found that worn bearings, giving the wheel a chance to vibrate in a vertical plane, sometimes resulted in a length of groove all out of proportion to what should logically be expected. For this reason a third bearing, on the outside of the grinding wheel, was added to the apparatus, as shown in Fig. 2. This has resulted in much smoother running and more consistent results.

It has been suggested that the temperature of the wheel has a decided influence on the rate of cutting. This has been tested out in the following way:

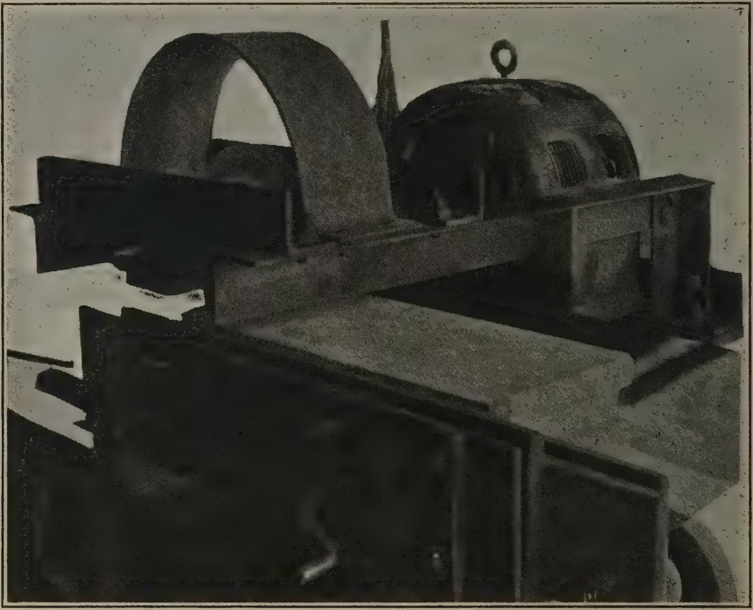

Fig. 2.

A cut was made on a number of tile, allowing the wheel to cool an hour or more between each cut, then cuts made on some of the first tile tested. Usually two cuts made on the same tile check up fairly closely. A second test was run, keeping the wheel in as continuous operation as possible by changing the tile very rapidly. After two hours' run, cuts were again made on the first few tile tested and the length of cut found to be as closely the same as when the wheel was allowed to cool between cuts. It is undoubtedly true that the temperature has a decided effect in the rate of cutting but it seems probable in this case that the surface of the wheel reaches a steady temperature within the first few seconds after starting the cut, so that continued cutting has very little influence. Tests were also made to determine the effect of dressing the cutting face of the wheel between each cut. With the particular grain and grade of wheel used this again seems to have comparatively slight effect.

After this method for determining the resistance to abrasion had been in use for some time it occurred to one of us that it might be possible to tie up with some other property of the silica brick; particularly with some property which required less elaborate apparatus and possibly one which could be used without destroying the tile tested. This latter idea has not yet been realized but the data given below do seem to show that resistance to abrasion is mainly dependent upon porosity and degree of firing.

The following brief description of methods used may not appear out of place.

Method Used in Determining Porosity

Samples are cut approximately to two-inch cubes, original surface being removed by grinding. The samples are heated, when necessary, to 110°C to remove the moisture and the dry weight (D) obtained to .10 gr. The samples are then placed in kerosene of known density (d) under a vacuum of 24 inches of mercury for four hours at 25°C, and then cooled down to room temperature while yet immersed.

When cool each test specimen is weighed, suspended in kerosene at 25°C to determine its suspended weight (S) in grams.

The saturated weight (W) is obtained immediately after obtaining the suspended weight by drying lightly with a kerosene moistened towel to remove excess kerosene, and then weighing in air.

The porosity (P) is obtained from the following equation:

$$P = \frac{W - D}{W - S}$$

The per cent water absorption (A) may also be obtained from the following equation:

$$A = \frac{W - D}{D \times d}$$

Method Used in Determining Apparent Specific Gravity

Samples are cut to about the size of a walnut, original surface being removed by grinding. The samples are then heated at 110°C to remove the moisture and the dry weight (D) obtained to .005 gr.

The weighed samples are placed in distilled water in a flask to which is attached a reflux condenser cooled by running water. The flask is then subjected to a vacuum of 24 inches of mercury and gradually heated until the water boils. After the samples have been boiled under this vacuum for one and one-half hours, they are allowed to cool to room temperature while still immersed.

When cool, each test specimen is weighed suspended in water to determine its suspended weight (S) and the temperature of the water is noted in order that its density (d) may be obtained.

The apparent specific gravity (sp. gr.) is obtained from the following equation:

$$\text{Sp. Gr.} = \frac{D}{D - S} d$$

Method Used in Determining Residual Expansion

A half brick of the nine-inch series, or about four inches cut from one end of a shape brick so as to obtain four measuring surfaces, is used. . Measurements are made with brick vernier calipers or the volume determined by displacement.

The test pieces are then placed in a gas-fired testing furnace and the temperature gradually increased, following a regular heating schedule, until 1450°C is reached. The temperature is then maintained as nearly constant as possible for seventy-two hours, after which the gas is shut off and the furnace kept closed and allowed to cool. After the furnace is cool the brick are removed and again measured with vernier calipers or by displacement. From the two sets of measurements the per cent change in size is calculated. This change in size, either linear or volumetric, is termed residual expansion.

The residual expansion may also be obtained from the apparent specific gravity data by using the curve developed by the authors.[1]

Some of the results on residual expansion given in this paper were obtained by the latter method because it is more rapid and there were a large number of tests to be made.

Data

Length of Cut The ability of a silica brick to resist abrasion does not appear to be dependent upon any one characteristic property of the brick but may be influenced by any one or more of the following properties: porosity, degree of burn, grind, quality of ganister, per cent lime, or workmanship (physical structure or bond). Each one of these properties seems to exert an influence, and no single one can be used as an accurate means of judging how a brick will behave when subjected to abrasion. It was found that measuring this resistance to abrasion by the abrasion test machine was the most sure and accurate way of judging this quality. In testing brick from any one manufacturer, made under the same process, the length of cut appeared, however, to vary fairly consistently with any one property, such as porosity, providing the other properties were approximately constant.

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[1] F. A. Harvey and E. N. McGee, "Testing Coke Oven Refractories," *Jour. Amer. Ceram. Soc.*, **4** [6], 474 (1921).

In general it may be said that the average length of cut in silca shape brick suitable for use in coke oven linings was about five inches with two minute grinding. If very hard and dense the cut was less, and if porous, poorly bonded, or underfired, the cut was longer. Fig. 3 shows some tile after testing.

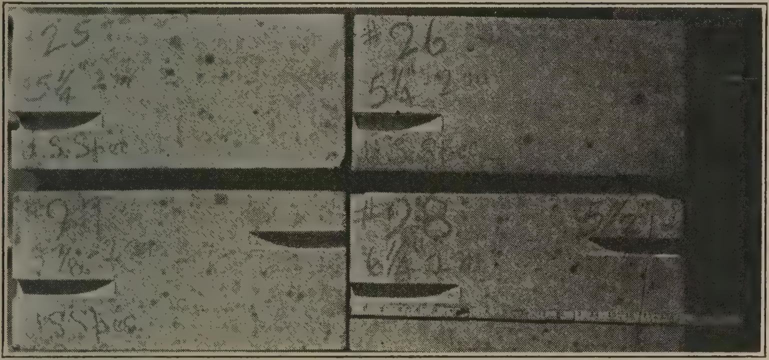

Fig. 3.

For comparative purposes a few tests were made on fire clay brick. The length of cut in clay brick, with two minutes of grinding, showed 6.6 inches for fairly soft burn, 4.5 inches for hard burn, and 1.4 inches for very hard burn. The following shows a comparison of these results with the porosity of the same brick:

Length of cut, inches	Degree of burn	Per cent porosity
6.6	Fairly soft	24.2
4.5	Hard	19.8
1.4	Very hard	16.9

Relation of Length of Cut to Physical Structure[1]

The approximate behavior of a silica brick in the abrasion test can be determined fairly accurately by visual examination of the physical structure after breaking, and by cutting into it with a small testing hammer having a sharp edge. If the brick is easily cut, or the visual inspection of the structure shows it to be quite loosely bonded, friable, too finely or too coarsely ground, it is quite likely to show a long cut on the abrasion test. Sometimes the skin surface is hard, but the internal structure is soft, consequently a surface inspection is not always adequate. It is impossible, of course, to draw a sharp line of distinction between brick by inspection, but an inspector can readily tell when the brick are hard and satisfactory or when they are too soft to be resistant to abrasion. If they are doubtful in this quality to resist abrasion, samples should be tested to determine more accurately this quality.

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[1] Hammer cut and breaking.

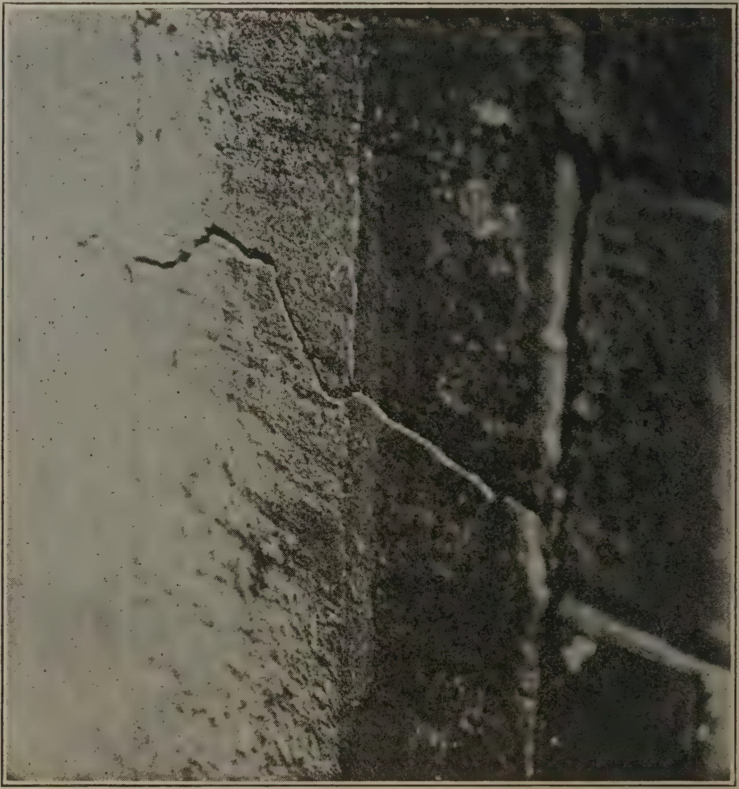

Fig. 4.—Showing abrasion on oven side walls.

Relation of Length of Cut to Porosity

Other properties being approximately the same, the length of cut in silica brick increased with the porosity. A long cut in some cases, in which the porosity was fairly low, could be attributed to the fact that the brick was too coarse or too fine. If too coarse, the grinding wheel had a tendency to pull apart the particles of ganister, instead of grinding through them. If too fine, the material did not seem to offer much resistance to the grinding wheel.

The following results show the relation between the length of cut and porosity and represents a total of approximately one hundred tests The brick were all made at the same plant, by the same process, and were all hard-fired brick. The various classes (A, B, C, etc.) are grouped according to the length of cut, for two minutes of grinding.

(A) represents the average of all cuts up to 3.5″
(B) between 3.5″ and 4.0″
(C) between 4.0″ and 4.5″
(D) between 4.5″ and 5.0″
(E) between 5.0″ and 5.5″
(F) between 5.5″ and 6.0″
(G) between 6.0″ and 6.5″
(H) all cuts above 6.5″

Class		Average length of cut, inches	Per cent porosity
A	Very hard	3.30	25.23
B	Hard	3.76	26.04
C	Hard	4.35	27.21
D	Fairly hard	4.73	27.64
E	Quite soft	5.24	27.97
F	Soft	5.73	28.21
G	Soft	6.28	28.78
H	Very soft (underfired)	9.74	29.06

(The term hard in this connection refers to resistance to abrasion while soft refers to lack of resistance, not to degree of firing.)

Averaging these results according to porosity instead of length of cut the following data is obtained:

Per cent porosity	Length of cut, inches	Per cent porosity	Length of cut, inches
24.7	3.56	27.8	4.69
25.8	3.81	28.3	5.00
26.3	3.81	28.8	5.59
26.9	4.31	29.1	5.31
27.3	4.25	29.7	5.19

The graph shown in Fig. 5 is obtained from the mass of data represented by these averages. It is not pretended for an instant that it is exact, even its shape may be somewhat in error for the high values. There are so many factors involved that it has been impossible to separate them except in a general way. Particularly at high values the outcome is usually the result of a combination of

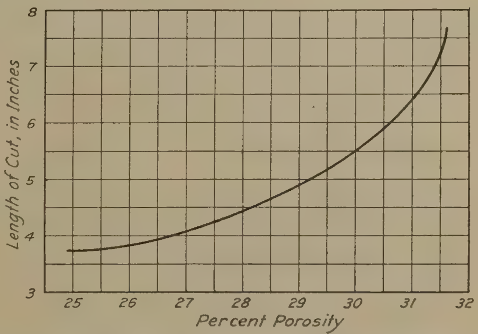

FIG. 5.—Approximate relation between length of cut and porosity.

the causes. We wish to be very emphatic in the caution against taking these values as standards. The results given are for tile made on one plant within a comparatively short period of time, and as such show reasonably consistent results. The change made in the testing apparatus as represented from Fig. 1 to Fig. 2 resulted in a decided decrease in the length of cut on tile apparently alike. Experience with the method extending over two years or more shows that the relation between porosity and length of cut is not absolute, particularly when brick from several plants and from different types of quartzite are under consideration.

The porosity test on one or two brick does not determine definitely how these brick will behave, either in service or on the abrasion test. On a large number of samples, made at the same time and at the same plant, such a relation does appear to exist. Experience has shown, however, that this test alone cannot be relied upon. No brick having a low porosity, 24% to 25%, has ever proved to be soft, but a brick with a porosity of from 28% to 30%, or even higher, may be hard and give satisfactory service.

The more experience we have with testing refractories the more we become convinced of the necessity for taking *all* the tests into consideration in judging of the final result.

Relation of Porosity and Burn to Modulus of Rupture

There is apparently no relationship between the porosity or burn and the modulus of rupture, as is shown by the following results:

	Per cent porosity	Apparent specific gravity	Modulus of rupture, lbs. per sq. in.
1	31.0	2.285	419
2	26.3	2.355	470
3	30.9	2.303	619
4	29.4		630
5	27.7		637
6	26.5	2.307	719
7	30.2		740
8	27.7	2.304	904
9	35.2	2.286	943
10	25.6	2.335	962
11	27.3	2.344	1083

Each of these results is the average of at least three tests on brick which were manufactured by the same process and from the same kind of ganister, and consequently gave very close results on the modulus of rupture test.

No tests were made to determine the relationship between the length of cut on the abrasion test and the modulus of rupture. In some cases, it would seem that they would be comparable, but not in others. The brick numbered (9) for instance, although they showed a high modulus of rupture, appeared to be soft and easily cut, while the bond was very good. It seemed probable, though, they would not be resistant to abrasion as measured by the abrasion test machine. Also brick labeled (2) looked as though they would be just as resistant to abrasion as brick labeled (7), yet they showed considerably lower results on the modulus of rupture test.

Relation of Length of Cut to Burn

The length of cut also appeared to vary quite consistently with the degree of burn as determined by the apparent specific gravity, or residual expansion. Hard-fired silica brick are usually resistant to abrasion, while underfired brick are soft and show a long cut on the abrasion test.

Class	Length of cut, inches	Apparent density	Per cent residual expansion
A	3.30	2.308	0.35
B	3.76	2.307	0.3
C	4.35	2.310	0.4
D	4.73	2.312	0.45
E	5.24	2.313	0.45
F	5.73	2.311	0.4
G	6.28	2.314	0.5
H	9.74	2.316	0.55
I (underfired brick)	10.30	2.375	1.95

These figures are undoubtedly complicated by other factors.

This test alone, moreover, is not sufficient for judging how resistant a brick is to abrasion. Brick which show a residual expansion of from .5% to 1.0% would be termed hard-fired and yet they may be very susceptible to abrasive action.

Effect of Refiring in Kiln

(A) Length of Cut Refiring silica brick in the kiln increases their resistance to abrasion, as determined by the abrasion machine, between 20% and 30%. A brick which was cut $14^1/_4''$ on the original burn showed a cut of $10^1/_4''$ after refiring, a decrease of 28%. Brick which were more resistant on the original burn showed a smaller increase in resistance after refiring.

(B) Porosity Refiring silica brick in the kiln decreases the porosity approximately 3%, as shown by the results in the following table.

The greater resistance of a silica brick to abrasion caused by refiring is more likely to be due to the formation of a hard skin surface and stronger bond, than to any appreciable change in porosity.

	Porosity, original brick	Porosity, after refiring	Per cent change in porosity
	30.6	30.7	+0.3
	32.1	31.3	−2.8
	30.1	29.8	−1.0
	26.2	25.1	−4.2
	27.9	28.0	+0.3
	30.3	29.3	−3.3
	32.6	31.3	−4.0
	29.6	28.8	−2.5
	29.3	27.1	−7.5
Average	29.7	28.9	−2.7

Relation of Length of Cut and Ganister

There appeared to be a marked difference between the behavior of brick made from Medina and Baraboo quartzite on the abrasion test. The Baraboo quartzite brick are of such character that they cannot be cut with the grinding wheel used, the material slagging under the heat of the wheel, thus preventing further progress. Some of the western brick which were tested had a very dead, "punky" ring and were of rather coarse texture, yet the length of cut was only one inch in two minutes of grinding. The test machine would undoubtedly have to be changed in some manner in order to make tests on these brick of any value.

Operating Experience

As is shown in the photograph of the coking chamber of a by-product coke oven (Fig. 4) there may be considerable abrasion on the side walls, due to the pushing of the coke, and on some brick this wear is quite marked. It seems to be mostly produced shortly after a new lining is installed. When the brick have been in use for some time, they become more and more resistant to this abrasive action. A careful check on brick put into service show that the abrasion test gives a fair indication of what can be expected of them relative to this abrasive action. Brick of soft structure, which show a cut of 8″ or 10″ in 2 minutes of grinding on the abrasion test, also show considerable wear when put into service, while those which only show a cut of 3″ or 4″ are resistant to abrasion in the oven. The result of this experience with eastern ganister brick would indicate that brick showing a cut of more than 5″ in 2 minutes, or at the rate of $2^1/_2$″ per minute in the particular apparatus used, would be unsatisfactory where abrasive action is important. The method of test has been in constant use for nearly two years and has resulted in the production of tile which are consistently more resistant to abrasion than those previously produced.

Mt. Union, Pa.

ARTIFICIAL SILLIMANITE AS A REFRACTORY.—PART II[1]

By Hewitt Wilson, Clarence E. Sims and Frederic W. Schroeder

Resistance of Refractories to Load at High Temperatures

Of the usual refractories, silica brick bears the distinction of being the only one capable of carrying loads such as those of the roof of the open-hearth steel furnace for continued service above 1500°C.

Silica brick contains a maximum of 6% fluxing material consisting of lime-aluminum silicates, 2% of which has been added as lime to the original quartzite rock. The rest of the impurities are scattered throughout the interiors of the quartzite grains. The lime-alumina-iron silicate flux is so well distributed throughout the silica brick structure and is so small in amount that on fusion, the flux cannot lubricate the adjoining grains, but can only form a liquid medium for solution, saturation, and recrystallization of the silica. In this manner, an interlocking crystalline structure is developed which will resist loads at high temperatures very close to the melting point of the crystalline material.

At the high melting point this crystalline structure disappears and the mass is amorphous. A petrographic examination of a silica brick after failure by shearing at cone 31 revealed no crystalline material.

When the same amount of impurities are added to pure quartz rock as a coating to the grains, the mineral inversions are delayed because of the lack of surface contact with flux and the excess of concentration of fluxes between the grains causes lubrication and early failure. A better method would consist of a very intimate and fine grinding of the flux with a portion of the quartz before adding to the coarse material. An excess of impurities, a low temperature of firing accompanied by an imperfect crystalline bond, or too sudden temperature changes causing the crystalline bond to be broken by rapid volume changes, will all cause early failure.

The permanent expansion of silica brick on heating, which is caused by the inversion of the silica minerals, is peculiar to silica brick alone, for all the other refractories tend to shrink after a certain low temperature temporary expansion period has passed. Fire clay and alumina refractories, manufactured by the usual methods, are composed largely of amorphous materials. The small amount of crystalline kaolinite present dissociates below 1000°C. Other crystalline silicates fuse or are rapidly dissolved by the surrounding fluxes. Crystalline sillimanite will form at the higher temperatures but not in sufficient quantities to provide a rigid crystalline framework. Hence, this amorphous aluminum-silicate mass, possessing no definite melting point but rather a fusion range, deforms at successively lower temperatures as the pressure is increased.

Magnesia and chrome brick with cone-fusion points far above that of silica brick are notoriously unable to carry load at the high temperatures. Magnesia brick will often contain over 15% and chrome brick over 40% of lime-iron-aluminum silicates, and hence are easily crushed under light loads at the softening temperatures of their silicate impurities. It should be possible to develop an interlocking crystalline structure of periclase or of periclase and magnesio-ferrite if high enough temperatures are used. Very little is known of the high-temperature crystallization of chromite.

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[1] For Part I see *Jour. Amer. Ceram. Soc.,* 7 [11], 842 (1924).

The commercial zirconia brick have been bonded with fire clay and naturally follow the load-test curve of the inferior member. Pure zircon, the monosilicate, may possibly be able to develop its own interlocking crystallization.

Refrax brick, made by recrystallizing silicon carbide brick in the electric furnace, is another example of the crystalline-bonded structure which will withstand loads at high temperatures up to the point of dissociation. When clay or amorphous materials are used as a bond, the softening of the brick varies directly with the amount and character of the amorphous bond.

Both the sillimanite and refrax brick of crystalline bond were able to resist the load of twenty-five pounds per square inch at higher temperatures than silica brick and therefore indicate ability to carry the loads required for metallurgical roof work. Resistance to slagging and ability to withstand temperature changes are the other questionable points.

Load-test failure by shear occurs in those brick consisting of a large quantity of more refractory grains or grog, with a small amount of bond which softens first and provides films of lubricant for adjoining grains. By increasing the amount of amorphous material, the failure becomes more gradual and with more preliminary shrinkage before rupture. With large amounts of amorphous material, the brick gradually shrinks to a very small height without cracking.

Spalling Tests

Loss in Weight and Loss in Strength

Both the water-quenched[1] and the air-cooled spalling test methods were used to compare the thermal shock resistance of sillimanite with other refractories. Better and more consistent results were obtained after heating one end of the brick to 1350°C, by cooling in a blast of air from the compressed air line. The brick were weighed after each cooling period and the results tabulated in the following table.

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[1] Nesbitt and Bell, *Proc. Am. Soc. Testing Mat.*, **16,** 369 (1916).

R. M. Howe and R. F. Ferguson, "A Study of Spalling," *Jour. Amer. Ceram. Soc.*, **4,** 32 (1921).

R. M. Howe and S. M. Phelps, "The Use of Plastic-Clay Grog in Preventing Spalling," *Jour. Amer. Ceram. Soc.*, **4,** 119 (1921).

TABLE II

SPALLING TESTS

Per Cent Loss in Weight after Air Cooling

Heating	1	2	3	4	5	6	7	8	9	10
Refrax	0	0	0	0	0	0	0	0	0	0
Fire clay	0	0	1	1	1	1	3	3	3	4
Alundum	0	3	7	7	8	51				
Chromite	0	0	0	33	33	33	53			
Sillimanite (stony)	1	3	23	25	26	44				
Zirkite	2	51								
Silica	11	43								
Sillimanite (glassy)	58									
Magnesite	64									

The stony type of sillimanite was superior to the glassy type in both tests and gave better results than zirkite, silica, and magnesia brick of commercial manufacture. The refrax brick developed a series of cracks which were plainly visible when the brick were red hot, but separate portions could not be removed by hand. The fire-clay brick were also resistant to spalling. This sample retained 96% of its original weight after ten treatments. Porous fire brick disintegrate slowly by crumbling; when vitrified, large portions spall off. The alundum and chromite brick were in the intermediate class.

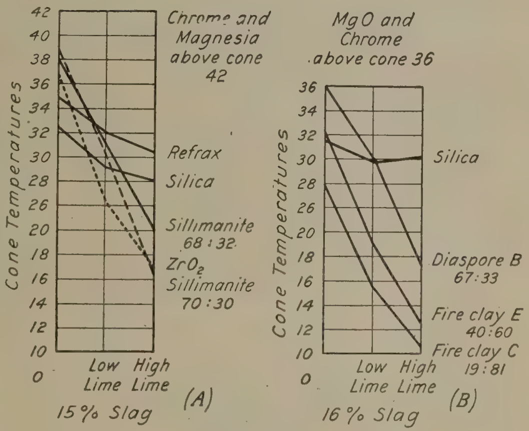

FIG. 10.

(*A*) The fluxing effect of lime as shown by the cone fusion slag tests on artificial sillimanite and other refractories.

(*B*) The fluxing effect of lime on silica, diaspore, and fire-clay brick. (R. M. Howe, "A Study of the Slag Test," *Jour. Amer. Ceram. Soc.*, **6**, 466(1923).)

Resistance to Spalling Determined by Loss in Compressive Strength

The brick were cut in half; one-half was crushed without heating, and the other half heated to 1350°C (cone 14). After holding at this temperature for one hour, it was withdrawn from the furnace and cooled on edge in quiet air for an hour and then replaced in the furnace. The brick were given two heatings and two quick coolings. The preliminary results are given in Table III.

Fire-clay brick unless nearly vitrified at 1350°C retain close to their full strength after two quick heatings and coolings in air. Both the silica and

TABLE III

Sample	No. heatings	Original crushing strength, lbs. per sq. in.	Strength remaining after heating	Notes
No. 2 fire clay	2	2709	72	One sample, nearly vitrified
Woodland fire clay	2	969	102	One sample
Silica	1	1345	0	One sample
Magnesite	1	3051	0	One sample
Refrax	2	5507	73	One sample, split in two halves
Zirkite	2	7363	100	Soap brick, only 2.6″ high. Cracked
Sillimanite-corundum	2	8190	59	One sample. Internal cracks

magnesite brick were total losses after a single quick heating. The refrax brick split in two parts after two heatings but the halves retained 73% of the original strength. The sillimanite brick, depending on the interlocking crystallization for bond, gave the highest crushing strength (8190 pounds per sq. in.) but retained only 59% of this strength after two heatings. However, it showed a better spalling resistance than either the silica or magnesia brick.

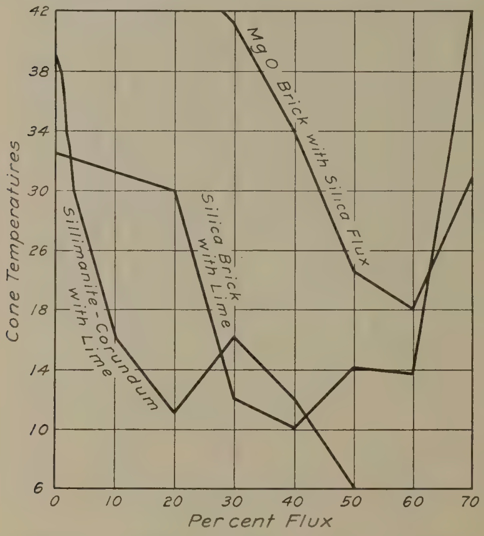

FIG. 11.—Fluxing effect of lime on artificial sillimanite-corundum brick and silica brick. The effect of silica on magnesia brick.

Slag Tests

Cone-fusion Method[1] This method consists of determining the cone fusion of various mixtures of the refractory and 60-mesh slag. The decrease in cone-fusion temperature from that of the original refractory is taken as a measure of the solvent action of the slag on the refractory. F. W. Schroeder[2] tried the following synthetic slags with sillimanite, and commercial refrax, silica, alundum, and zirkite brick, all ground to pass 100-mesh.

When the results in Table V are plotted against oxygen ratio, silica, alumina, iron oxide, or manganese content of the slags, no definite re-

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[1] R. M. Howe, "A Study of the Slag Test," *Jour. Amer. Ceram. Soc.*, **6**, 466 (1923). Also Howe, Phelps, and Ferguson, "The Action of Slag on Silica, Magnesite, Chrome, Diaspore and Fire-Clay Refractories," *Jour. Amer. Ceram. Soc.*, **6**, 589 (1923).

[2] F. W. Schroeder, fellow, Univ. of Wash., in coöperation with U. S. Bureau of Mines, 1922–23.

TABLE IV

COMPOSITION OF SYNTHETIC SLAGS

	1 Blast furnace	2 Heating furnace	3 Open hearth basic	4 Open hearth acid
Silica	38.4	39.5	20.0	50.3
Alumina	13.5	7.1	4.2	5.9
Iron oxide	1.6	50.5	15.6	31.7
Lime	43.0	1.5	47.7	2.3
Magnesia	2.4	0.8	7.0	0.0
Manganese	1.1	0.6	5.5	9.8
	100.0	100.0	100.0	100.0

TABLE V

CONE FUSION OF VARIOUS REFRACTORIES CONTAINING 15% SLAG

Slag No.	0	1	2	3	4
Chromite brick	...	..	...	..	...[a]
Silica brick	32–33	28	28	28	29–30
Zirkite brick	37	16	27	18	26
Alundum brick	39–40	23	27–28	27	27–28
Refrax	35[b]	31[b]	32[b]	30[b]	32[b]
Sillimanite—Melt No. 28	39	18	26	15	35
Sillimanite—Melt No. 41[c]	38	20	29	20	33

a All the chromite mixtures deform above cone 42.

b Indicates rapid dissociation.

c Alumina-silica ratio, 68:32.

lationships are noted. Plotted against the lime content, the curve shows that the activity is the greatest in the slags of high-lime content for all refractories save the chrome and magnesia. This likewise holds true for the sum of the lime and magnesia. As these commercial slags are rather complicated mixtures, comparisons between slags varying but little in lime content show irregularities. The two low-lime slags (Nos. 2 and 4) were therefore combined for one point, and the two high-lime slags (Nos. 1 and 3) for the second point on the curves. (Fig. 10*A*.)

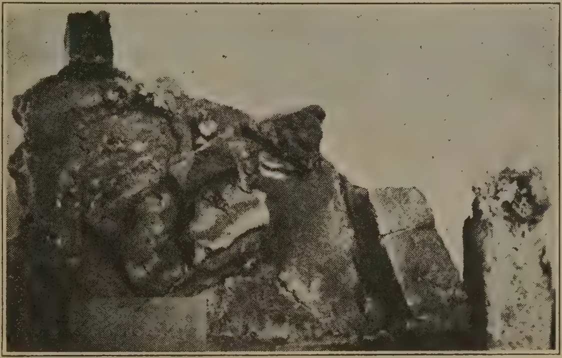

FIG. 12.—Bath slag test No. 1. A portion of the magnesia side walls, and the frozen basic slag containing the softened magnesia brick in the center. The silica brick has been entirely dissolved and the sillimanite-corundum brick standing at the right was pulled from the upper left of the bath at the end of the run.

It is noted that the silica was noticeably less affected by slag than either of the two sillimanite samples. Also, that high lime and low lime caused but little difference with the silica but was a very important factor with the two sillimanite and the zirkite samples. Howe's data[1] given in Fig. 10*B* show similar results in comparing silica brick with the high-aluminous diaspore and two grades of fire-clay brick. It is to be expected from the CaO-Al_2O_3-SiO_2 concentration diagram that mixtures of these three components should fuse at lower temperatures than the lime-silica mixtures. Ternary eutectics are found with melting points as low as 1165° and 1265°C while the binary eutectic between lime and silica is 1436°C.

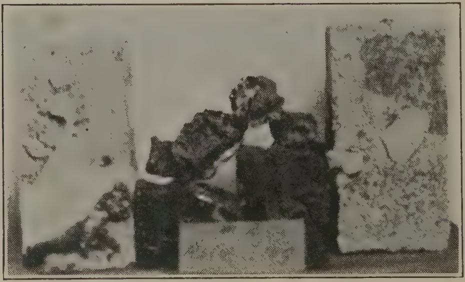

FIG. 13.—Bath slag test No. 2. Acid slag. The silica and artificial sillimanite-corundum brick, left and right, respectively, have been affected but little, while the magnesia brick in the center has been badly attacked.

Because of the complicated character of the commercial slags and as lime is one of our most active high-temperature fluxes H. C. Fisher[2] made a cone-fusion study of magnesia, silica and sillimanite mixed with lime and a few simple mixtures of lime and silica.

TABLE VI

CONE-FUSION SLAG TEST OF SILLIMANITE WITH LIME

Melt No. 28. $Al_2O_3 : SiO_2 : 70 : 30$

Per cent lime	0	0.5	1.0	1.5	2.0	2.5	3.0	10.0	20.0	30.0	40.0	50.0
Cone fusion	39	39−	36−	36½	34−	33	30−	16	11	16+	12	6+

TABLE VII

CONE-FUSION SLAG TEST OF SILLIMANITE, MAGNESIA, AND SILICA WITH 20% LIME-SILICA MIXTURES

Slag composition......	SiO_2	0.0	100.0	75.0	50.0	25	0
	CaO	0.0	0	25	50	75	100
Magnesia brick.........		All above cone 42					
Silica brick..........		32	32	31+	31	30½	30
Sillimanite No. 28.....		39	37+	34	17−	11−	11

TABLE VIII

CONE-FUSION SLAG TEST OF MAGNESIA WITH SILICA

Per cent SiO_2	0	10	20	30	40	50	60	70
Cone fusion	Above cone 42			41–42	34	20–23	18	31

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[1] "A Study of the Slag Test," *loc. cit.*

[2] H. C. Fisher, fellow, Univ. of Wash., in coöperation with U. S. Bureau of Mines, 1922–3–4.

TABLE IX

CONE-FUSION SLAG TEST OF SILICA WITH LIME

Per cent lime	0	20	30	40	50	60	70
Cone fusion	32–33	30	12	10	14+	14−	Above 41

TABLE X

CONE-FUSION SLAG TEST OF SILLIMANITE-CORUNDUM WITH Fe_2O_3-CaO IN THE PROPORTION OF $1Fe_2O_3$ TO 1CaO BY WEIGHT. MELT NO. 28

Per cent CaO-Fe_2O_3..........	0	1.0	2.0	4.0	6.0	8.0	10.0	20.0	30.0
Cone fusion.................	39	38+	35	30½	19−	15	14	11	6

TABLE XI

CONE-FUSION SLAG TEST OF SILLIMANITE-CORUNDUM WITH Fe_2O_3. MELT NO. 29

Per cent Fe_2O_3	0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0	10.0	20.0	30.0
Cone fusion	38	37½	36½	35	34−	32½	29	26	20–23	14	10	9

From these seven studies and the accompanying charts (Figs. 10 and 11), it is noted that the fluxing effect of small amounts of lime is greater with sillimanite than with silica. Three per cent lime brought the fusion point of sillimanite from cone 39 to cone 30 and 50% to near cone 6. A rise in the curve at 30 to 40% lime is apparently due to the influence of the gehlenite elevation.[1] Larger amounts of lime reduced the fusion of silica and 40% CaO brought it down to cone10. Or, in other words, with an excess of slag, the fluxing effect of lime should be very similar on both sillimanite and silica brick. Lime had but little effect on the magnesia but 60% silica reduced the cone fusion to cone 18.

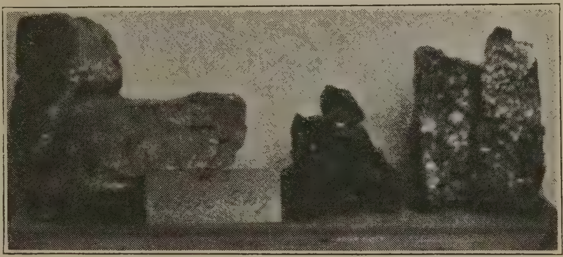

FIG. 14.—Bath slag test No. 3. The relative action of the high-lime slag on an artificial sillimanite-corundum brick (right) and the magnesia brick (center). The silica brick was entirely dissolved. At the left is a portion of the slag bath showing how it attacked the magnesia side wall.

Bath Method The cone fusion slag method is an excellent way to determine the effect of the chemical activity of the slag when in intimate contact with the refractory, but in order to determine the resistance offered by the structure of the brick, various refractories were exposed to a bath of slag. The penetration of the slag will depend on the surface exposed, the porosity of the structure, and the fluxing power of the slag on both the large grains and their bonding material. If the bond is easily attacked, the structure is quickly reduced to loose grains. If an intergrowth of crystalline material binds crushed fragments of the same crystalline composition to a dense structure of minimum absorption, the maximum resistance of that material has been found. The resistance of a brick made of crushed fragments bonded with glass depends on the resistance of the glass bond. Amorphous materials should have less resistance than crystalline.

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[1] G. A. Rankin and F. E. Wright, "The Ternary System CaO–Al_2O_3–SiO_2," *Am. Jour. Sci.*, **39**, 40 (1915).

Silica, magnesia, and sillimanite-corundum brick were placed in baths of the following slags:

TABLE XII

COMPOSITION OF SYNTHETIC SLAGS

	1 Basic slag prepared	2 Basic slag open hearth	3 Acid slag prepared
CaO	62.2	44.0	20.0
Silica	15.9	13.2	70.0
Alumina	18.0	4.2	10.0
Fe_2O_3	....	20.9	....
Magnesia	....	9.9	....
Manganese diox	....	7.8	....
F_2	3.9	....	....
	100.0	100.0	100.0

The slag was placed in 12 x 12 x 9-inch pots of various refractory material in an oil-fired furnace. A series of experiments with temperature variations from 1500 °C to 1600 °C and time variations from 13 to 24 hours gave the following general results.

TABLE XIII

BATH SLAG TESTS OF SILICA, MAGNESIA, AND SILLIMANITE-CORUNDUM BRICK

Test No. 1. Basic slag No. 1. Total time, 20.5 hrs. Temp. 1550–1570 °C for 7.5 hrs. Fig. 12

	Silica	Magnesia	Sillimanite-corundum
Time of failure	16–18.5 hrs.	17–18 hrs.	None
Type of failure	Entirely dissolved	Softened, spalled solution of small pieces	Base eaten
Per cent remainder	0.0%	Not separable from slag	85%

Test No. 2. Acid slag No. 3. Total time, 20.5 hrs. Temp. 1550–1570 °C for 7.5 hrs. Fig. 13

	Silica	Magnesia	Sillimanite-corundum
Time of failure	....	20.5 hrs.	....
Type of failure	....	Solution, spalling, softening	....
Per cent remainder	100%	93.5% including slag Small pieces	100%

Test No. 3. Basic slag No. 1. Total time, 13 hrs. with slag. Temp. 1475–1530°C for 8 hrs. Fig. 14

Time of failure	7.5 hrs.	13 hrs.	13 hrs.
Type of failure	Complete solution	Softening, spalling solution of small pieces	Bottom eaten until brick fell
Per cent remainder	0.0%	52%	53%

Test No. 4. Open-hearth basic slag No. 2. Total time, 13+ hrs. Temp. 1475–1530°C for five hrs. Fig. 15

Time of failure	7.5 hrs.	11.5 hrs.	Standing at end
Type of failure	Complete solution	Softening, spalling and solution of small pieces	Bottom eaten
Per cent remainder	0.0%	25%, small pieces	80%, one piece

Test No. 7. Iron oxide slag. Maximum temp. 1530–1537°C for two hrs. Hours with slag 9.5, total hrs. 19.5. Fig. 16

	Sillimanite corundum	Zirconia	Silicon carbide
Time of failure	None	8 hrs.	None
Type of failure	Slightly eaten at base	Softened and disintegrated	Eaten badly at base
Per cent remainder	95%	50%	95%−

1. As shown in Table XIII, a silica brick standing on end in a 4-inch bath of both basic slags entirely dissolved before the magnesia brick softened or spalled enough to give way or the sillimanite-corundum brick had its base eaten. (Figs. 12, 14, and 15.)

2. In the acid slag both the silica and sillimanite-corundum brick were far superior to the basic magnesia brick. (Fig. 13.) In all these tests the magnesia brick have had a handicap of spalling with the quick heating and in this way the surface exposed to the slag has been increased. Nevertheless, when standing on end and heated on all sides with no slag present, the magnesia brick will slump and split longitudinally above cone 30 under their own weight, showing that the silicate bond will not stand the high temperatures. As magnesia is not affected materially at these temperatures by the action of lime, the disintegration of the magnesia brick in slag is undoubtedly caused by the fusion of its silicate bond together with the low resistance of the latter to the slag.

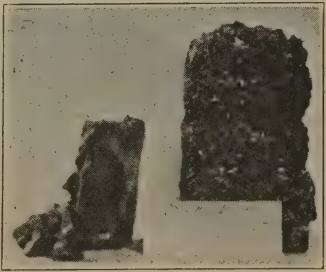

Fig. 15.—Open-hearth basic slag test No. 4. The silica brick was entirely dissolved while 80% of the artificial sillimanite-corundum brick (right) and only 25% of the broken magnesia brick remain.

3. The artificial sillimanite-corundum brick are able to maintain their rigidity under load at high temperatures even better than the silica brick and have less internal pore space for slag penetration, together with a moderate resistance to spalling, which, while it is not as good as some of the other refractories, is distinctly better than the silica or magnesia brick. Hence, although lime attacks both the silica and sillimanite readily, as shown by the cone-fusion slag tests, sillimanite-corundum brick were produced with a far better structure and less exposed surface which enabled the latter to lose only 25% while the silica brick lost 100% weight in a lime slag bath.

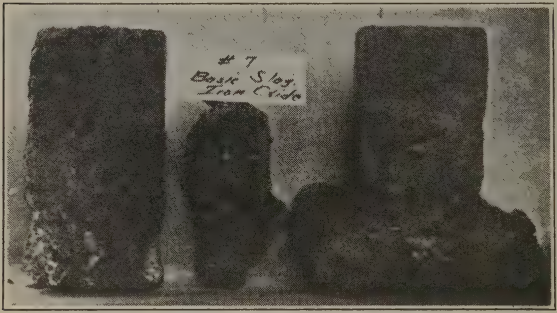

Fig. 16.—Iron-oxide slag test No. 7. Sillimanite, left; zirconia, center; and silicon carbide, right.

Several service tests have been made in the walls of a basic open-hearth steel furnace and in the roof of an electric iron furnace. In these positions a few sillimanite-corundum brick of laboratory manufacture have been surrounded with commercial silica brick. Both good and poor comparative results have been obtained. The chief difficulty was found in the spalling of the dense sillimanite-corundum structure in the repeated heatings and coolings, especially after the silica brick had receded and left the sillimanite-corundum brick projecting with five faces exposed. It is difficult to produce enough of these brick with laboratory apparatus for a large-size test and also to prevent the tendency towards brittleness in the fast cooling of the small kilns.

TABLE XIV

POROSITY OF VARIOUS REFRACTORIES

Refractory	Per cent absorption by weight	Per cent apparent porosity by volume
Carbofrax	5.2	12.2
Sillimanite-corundum	7.3	17.1
Silica	13.0	23.4
Zirconia	6.8	25.0
Chrome	13.4	25.6
Spinel	10.1	25.7
Average fire clay	15.1 (11.4–20.6)	28.1 (22.0–34.8)
Magnesite	14.3	32.9
Refrax	19.4	35.8

Summary

The results from the laboratory tests would indicate:

1. Sillimanite-corundum brick will withstand higher direct temperatures than the present silica, magnesia, chrome, fire clay, and zirconia brick.
2. Brick made from sillimanite-corundum mixtures, having the interlocking recrystallized structure will resist load at high temperatures better than any of the common refractories except refrax and better than the sillimanite-glass brick.
3. Though hard and dense, they will resist spalling better than silica and magnesia brick but are distinctly inferior to the ordinary fire-clay brick in this respect. A more open porous structure may be developed for conditions where resistance to spalling is essential and a high resistance to load at high temperatures is not essential.
4. Sillimanite-corundum brick will resist acid slags. While attacked by basic slags badly in the cone-fusion slag test, the brick structure can be made so dense that a greater resistance is produced than that of the open porous silica brick.
5. When lime as an impurity in sillimanite exceeds 1.5% it becomes a serious factor in reducing the fusion temperatures.

NOTE: We wish to acknowledge the kind assistance of the following co-workers: Clyde E. Williams, superintendent of the Northwest Experiment Station, U. S. Bureau of Mines, for general supervision and advice; E. P. Barrett, J. D. Sullivan, and A. E. Anderson of the Northwest Experiment Station, U. S. Bureau of Mines, for chemical analyses, and G. E. Goodspeed, of the University of Washington for petrographic examinations. A. L. Bennett, formerly fellow, University of Washington, also did considerable preliminary work in the preparation of sillimanite refractories.

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Discussion

MR. GREAVES-WALKER: In attempting to find the silica-alumina ratio which would produce refractories having the best physical qualities, from a diaspore, we ran the gauntlet of raw materials having alumina contents ranging from 50% to 85%. We found invariably, that when we used a single material or a mixture that would produce a finished product containing approximately 63% Al_2O_3, we got the best combination of physical properties it was possible to obtain from a high alumina refractory. There would seem to be no question, therefore, that the sillimanite ratio produces a very superior product.

MR. PHELPS: Will Prof. Wilson elaborate a little bit on his method of forming that material, that is, the method of making the brick and also the method of preparing the material: whether the materials were ground or not, etc.

PROF. WILSON: This material is the result of electric fusing. We started out by using commercial materials, but in order to tie the thing down to pure product we used English china clay corresponding as closely as we could get it, and purified aluminum oxide, using various mixtures of this china clay and aluminum oxide. Cone 16 is the point at which most refractories start failing under load if they have present a certain amount of quartz glass. In producing any of these electrically fused products it will be necessary to have enough of some other oxide present to take up all of the silica in order to get a good product.

DR. PRATT: Did you use any of the natural mineral sillimanite?

PROF. WILSON: No.

DR. PRATT: In your resultant product you stated that there are crystals nearly an inch long. Did you analyze them to see whether they were sillimanite?

PROF. WILSON: Dr. Bowen, a few months ago, analyzed crystals in order to get as pure a crystal as possible and he found that such materials corresponded very closely to that given for sillimanite.

DR. PRATT: If I understood it correctly you stated you got the best results when you had sufficient alumina in your mass so that the resulting mass showed not only this mineral but also the crystals of corundum.

PROF. WILSON: If somebody can give an explanation of why that small amount of crystals will cause the crystallization of the sillimanite into the mica crystal form, he will be rewarded. We have explained it by the fact that possibly it is because the sillimanite crystals start growing, the plate of corundum comes out on top and prevents a growth.

DR. PRATT: Did the corundum crystallize out first?

PROF. WILSON: No, I think not. The only evidence we had was that on top of the tiny sillimanite crystals was a plate or film. A great many crystals of sillimanite had a plate of corundum riding on top.

ERRATA

W. E. Rice and R. A. Sherman, "Determination of the Distribution of Heat in Kilns Firing Clay Wares," 7[10] 748 and 749 the formulas should read:

$$H = 1543\left[\left(\frac{t_2 + 460}{1000}\right)^4 - \left(\frac{t_1 + 460}{1000}\right)^4\right]$$

$$\text{instead of } H = 1543\left[\frac{(t_2 + 460)^4}{1000} - \frac{(t_1 + 460)^4}{1000}\right].$$

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